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FOREWORD

This technical session was sponsored jointly by the Cane Sugar Refining Research Project, Inc. and the Southern Regional Research Center, U.S. Department of Agriculture. The program was assembled by Dr. Frank G. Carpenter and Dr. Margaret A. Clarke. The Conference Coordinator was Shirley T. Saucier assisted by Beverly S. Ballina.

This is one of a series of technical sessions held every other year to provide for an exchange of information among technical leaders in the cane sugar industry, and to report on research and recent developments of benefit to the cane sugar refining industry.

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THE ACTIVATION OF BONE CHARCOAL BY THERMAL AND CHEMICAL TREATMENT PART II. THE EFFECTS OF CHEMICAL TREATMENT

By J. Colin Abram and Michael C. Bennett[1]

(Presented by J. Colin Abram)

ABSTRACT

The first part of this paper dealt primarily with the structural changes which occur in bone charcoal at high temperatures.

An adsorbent, however, is described not only by its structure or the extent of surface available to any particular adsorbate molecule, but also by the nature, chemistry or activity of that surface.

An examination of the carbon and hydroxyapatite surfaces of bone charcoal by chemical treatment techniques has provided evidence for specific activation of both component surfaces.

INTRODUCTION

In the first part of this study (1) the structural changes which occur when bone charcoal is heated at elevated temperatures were discussed. In general, all the chars studied showed reductions in total surface area as the kilning temperature increased, but still exhibited gains in decolorising activity when washed free of the calcium hydroxide formed at the elevated temperatures.

In addition to the loss in surface area, there was an overall reduction in total pore volume as might be expected. Detailed analysis revealed that the loss in pore volume occurred essentially in pores with entrance diameters less than 40 nm. The pore volume in pores with entrance diameters greater than 40 nm actually increased. These observations led to the theory that the loss in surface area took place in pores which were too small to accommodate colorant molecules, while the gain in macropore volume may have provided increased accessibility to the useful surface.

The capacity of an adsorbent is not necessarily described by the extent of its surface accessible to any particular adsorbate molecule. It also depends to a large degree on the nature, chemistry or activity of the surface and the interaction between that surface and the adsorbate molecules.

This paper presents an account of certain chemical treatments which have provided evidence for specific activation of both carbon and hydroxyapatite surfaces and an indication of the specificity of sites for impurity adsorption.

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1. High temperature kilning

It is unlikely that any specific activation of the hydroxyapatite surface occurs when bone char is heated over the range 400°C to 900°C other than the removal of adsorbed Ca^{++} ions by incorporation into the surface structure at temperatures around 500°C, and the removal of $SO_4^{=}$ ions by reduction to organic sulphur species, a process which is complete at 700°C.

This view is confirmed when the hydroxyapatite surface areas, determined by the adsorption of sodium di-2-ethylhexyl sulphosuccinate from benzene solutions, of chars kilned between 400°C and 1000°C are compared with the capacity of those surfaces to adsorb Ca^{++} ions from calcium sulphate solutions. This is illustrated for a new char and a Thames fine grist stock char in figures 1 and 2 respectively.

It is possible, however, that some specific activation of the carbon surface has occurred by partial oxidation.

The importance of the role played by the carbon surface in bone char is often underestimated.

In order to examine the relative importance of the carbon and hydroxyapatite surfaces, samples of a stock char were decarbonised under controlled conditions. Each sample of char was heated for a total of two hours at 500°C in a nitrogen/oxygen atmosphere, progressive decarbonisation being achieved by increasing the proportion of the time in oxygen.

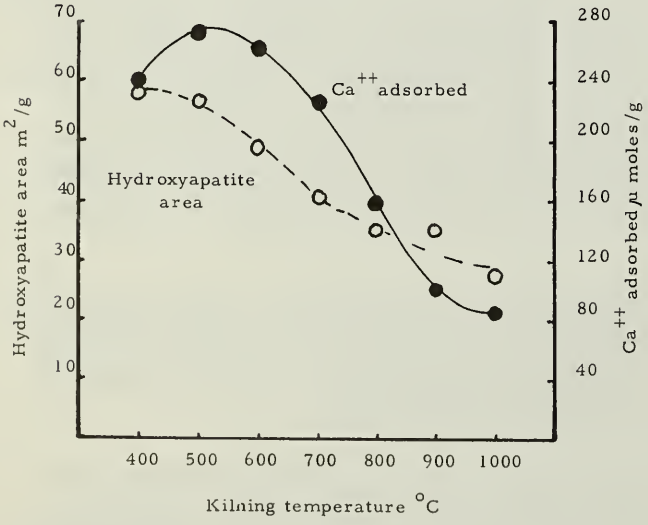


FIGURE 1. The hydroxyapatite surface area and corresponding Ca^{++} ion adsorptive capacity for a new char.

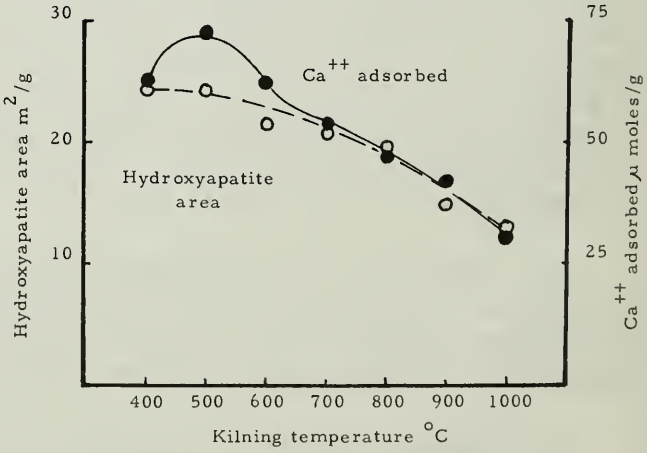


FIGURE 2. The hydroxyapatite surface area and corresponding Ca^{++} ion adsorptive capacity for a Thames' fine grist stock char.

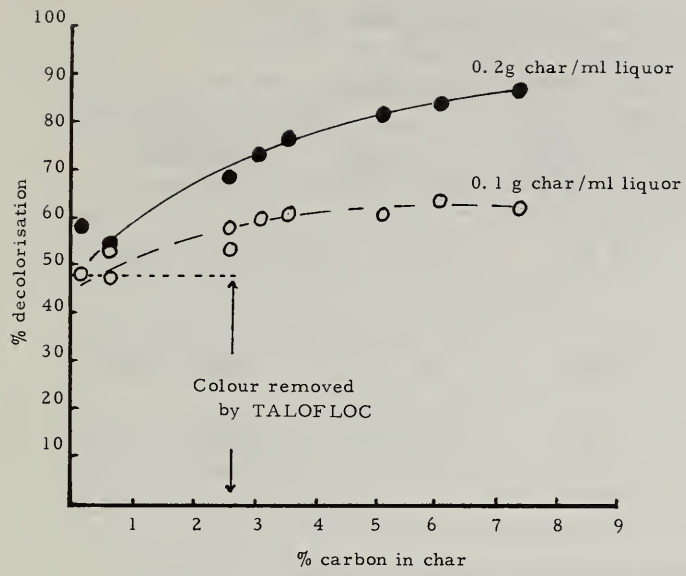


FIGURE 3. Decolorisation by decarbonised stock char.

The decolorisation capacity of the individual decarbonised samples was determined by measuring the degree of colour removed by 10 g char from 100 ml 65° Bx carbonatated liquor at 75°C after four hours contact time.

The results are presented in figure 3.

They show that with zero (extrapolated) carbon present the hydroxyapatite surface is still capable of removing 40-45% of the original colour present in the particular liquor used. As the % carbon present in the char increases so the colour removal increases to a plateau value of 60-63% at 5% carbon.

When the experiment was repeated using 20 g char per 100 ml carbonatated liquor, the effect of the carbon surface became more apparent.

At zero carbon content the colour removed was unchanged at 40-50%, but as the % carbon in the char increased, a vast improvement in decolorisation capacity was seen.

The experiment illustrates the importance of the carbon surface for the adsorption of that fraction of the colour which is least readily adsorbed, and which almost certainly emerges first from a column or cistern of char.

It also illustrates that, with the particular liquor used, there is insufficient colour of the type adsorbed by the hydroxyapatite surface present to saturate that surface.

It is interesting to note that the decolorisation achieved by decarbonised char could also be achieved by precipitation with TALOFLOC (2). This is an important result and confirms the widely held view that it is the strongly charged anionic colorant which is most readily adsorbed by the hydroxyapatite surface of char.

TABLE 1 Effect of exposure of freshly kilned char to atmosphere on the capacity of the char to remove Ca^{++} and $SO_4^{=}$ from Ca SO_4 solutions.

Exposure Time	0	5 min.	15 min.	1 hr.	4 hrs.	120 hrs.
Ca^{++} capacity μ moles/gm	72	75	83	70	75	75
$SO_4^{=}$ capacity μ moles/gm	89	68	58	58	48	44
% decolorisation	63	-	-	75	75	76

2. Exposure of char to atmosphere: concerning the adsorption of carbon dioxide.

When freshly kilned char is exposed to the atmosphere, the pH of the liquor off is reduced considerably. This has been explained in terms of the adsorption of CO_2, which on subsequent contact with water, disassociated into bicarbonate ions giving a reduced pH in the environment.

It has been shown by electrophoresis measurements that carbonate ions are more strongly adsorbed on char than sulphate, and it is therefore to be expected that the appearance of ionic carbonate species in equilibrium with char will have an effect upon the capacity of the char for Ca SO_4 adsorption. This is probably an effect associated with the hydroxyapatite rather than the carbon surface.

The effect is illustrated in Table 1, which shows the capacity of a char for Ca^{++} and $SO_4^{=}$ ions respectively after exposure to atmosphere for varying times after kilning.

The maximum capacities of the Ca^{++} and $SO_4^{=}$ ions were determined by measuring the removal of Ca^{++} and $SO_4^{=}$ ions from Ca SO_4 solutions after contact with char and applying the Langmuir model isotherm calculation.

It can be seen that the capacity of the char for Ca^{++} ions remains constant while the $SO_4^{=}$ ion capacity decreases with increased exposure to carbon dioxide. This effect almost certainly accounts for discrepancies between Ca^{++} and and $SO_4^{=}$ capacities which arise when no attempt is made to control the exposure conditions for char after kilning.

The decreased capacity of $SO_4^{=}$ ions is accompanied by an increase in decolorisation capacity determined by bottle shaking or column tests. The result again suggests that the ash removal function of char is not directly associated with its colour removal function, and draws further attention to the activated carbon surface as determining decolorisation activity.

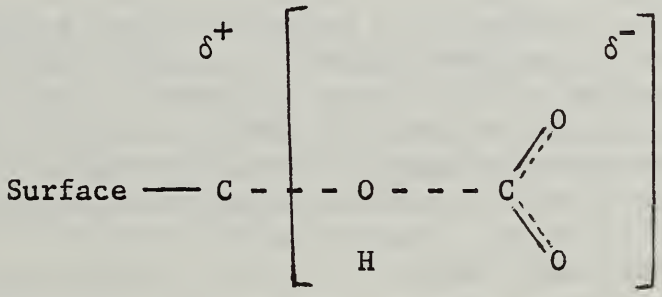
The activation produced by exposure to atmosphere CO_2 is not understood, but some light may be thrown on the problem by the following considerations:

TABLE 2 Decolorisation by CAL as a function of CO_2 absorption.

Treatment after kilning	CO_2 adsorbed ≡ moles CO_3 displaced	% colour removal	liquor pH after adsorption
Quench in water	48	75	7.6
Cool in N_2, air at room temperature	85	79	7.7
Cool in N_2 to 100°C CO_2 at 100°C to room temperature	199	85	8.0

i the effect of electrolytes on liquor decolorisation and on the surface potential of char shows that a positive charge favours decolorisation

ii adsorption of CO_2 as a surface complex of the form



has been indicated for both bone char and other carbons (3).

It is noted that the CO_2 complex tends to confer a positive charge on the carbon surface at which it is adsorbed.

iii the carbon surface is sensitive to pH and acquires a positive charge by adsorption of H^+ ions from environments of low pH.

The effect of pH on the decolorisation activity of granular carbons of the CAL type is well known, but attempts to illustrate the effect with bone char have always proved to be inconclusive because of the strong buffering action by the mineral components of the char.

It has been possible, however, to show an activation of the carbon surface of CAL type carbon involving an up-take of CO_2 and an increase in pH.

Samples of activated CAL type carbon were kilned at 800°C for one hour in nitrogen. One sample was quenched in water, the second was cooled in nitrogen and finally exposed to air at room temperature, and the third was cooled to

100°C in nitrogen, from 100°C to room temperature in CO_2 and finally exposed to atmosphere at room temperature. The amount of CO_2 adsorbed by each was determined and the decolorising capacity measured in bottle shaking tests. The results are shown in Table 2.

These results support the view that, when bone char is exposed to atmosphere, CO_2 is taken up in two forms

(a) a form which generates bicarbonates at the hydroxyapatite surface, reducing the capacity of the char for $SO_4^{=}$ ions, and a low pH on contact with water

(b) a form which is attached to the carbon surface and activates that surface with respect to colorant adsorption probably by the generation of a positive charge on the carbon surface.

3. The effect of sodium phosphate

Electrophoresis studies (4) have shown that char adsorbs phosphate ions much more strongly than $CO_3^{=}$ and $SO_4^{=}$ ions and it is therefore to be expected that PO_4^{3-} would displace any adsorbed $CO_3^{=}$ or $SO_4^{=}$. The adsorption of PO_4^{3-} from Na_3PO_4 solutions and concomitant release of $CO_3^{=}$ and $SO_4^{=}$ has been studied in the four chars identified in Part I of this paper (1).

The PO_4^{3-} adsorption isotherm on a refinery kilned sample of Thames' fine grist stock char tends to a plateau value, but a sharp rise above 50 mM initial concentration is indicative of multilayer formation. The $CO_3^{=}$ and $SO_4^{=}$ ions desorbed also tend to plateau values, but these are lower than the total carbonate and sulphate content of the char as determined by chemical analysis. In the case of Plaistow E and Liverpool M Stock chars nearly all the sulfate can be displaced by 30 mM Na_3PO_4, indicating differences in the location of the sulphate content of these chars.

The phosphate treatment has clearly removed adsorbed $SO_4^{=}$ and $CO_3^{=}$ ions, but far from leaving a "clean" surface, has deposited a layer of PO_4^{3-} ions. Taking the plateau value for phosphate adsorption to be 156 μ moles/g for Thames' fine grist char, and the radius of the phosphate to be 3.0 Å(5), the area occupied by the adsorbed phosphate in a square-packed monolayer would be 34 m^2/g. According to adsorption from solution data presented in Part I, the hydroxyapatite surface of this char (400-500°C) is 24 m^2/g and the carbon surface is 34 m^2/g: it is of course unlikely that the adsorption of phosphate ions is confined to the carbon surface, yet the result shows that some adsorption must occur here.

It was of interest to examine the liquor decolorisation and particularly the ash removal properties of chars treated with Na_3PO_4, but it was thought necessary first to remove the adsorbed PO_4^{3-} ions. A sample of the Thames char was therefore treated with 30 mM Na_3PO_4 solution and then washed with CO_2-free water until no more PO_4^{3-} could be detected in the wash water: at this stage, only 10% of the total PO_4^{3-} adsorbed had been removed. As a further attempt to remove the PO_4^{3-} ions, the washed char was kilned at 600°C in the temperature range where the incorporation of calcium ions into the hydroxyapatite surface structure is complete. The water-washed and kilned chars were then tested for

TABLE 3 The adsorptive capacity of chars treated with Na_3PO_4.

Treatment	Char A:- Refinery kilned stock char	Char B:- Char A, treated with 30 mM Na_3PO_4, water washed	Char C:- Char B, kilned 600°C/1 hr./N_2
Ca^{++} capacity μ moles/g	53	91	104
$SO_4^{=}$ capacity μ moles/g	58	154	88
% colour removal	75	63	69
% ash removal	10	87	84

$CaSO_4$ capacity, liquor decolorisation and ash removal; the results are compared with those for the original char in Table 3.

The ash removal properties of Char B are quite outstanding and are mostly retained after kilning in Char C. Since no phosphate ions were released during the $CaSO_4$ adsorption measurements, it would appear that the adsorbed phosphate ions are themselves the sites for ash removal. The enhanced $SO_4^{=}$ capacity shows that ash removal proceeds by ion-pair adsorption and is not selective for Ca^{++} ions as might have been expected. Indeed Chars B and C will adsorb a further quantity of phosphate if treatment with 30 mM Na_3PO_4 is repeated.

The liquor decolorisation results in Table 3 are very important, for here is an example of activation with respect to ash removal accompanied by deactivation with respect to colour. The results suggest that ash removal by ion-pair adsorption is independent of the processes which regulate colorant adsorption, though the latter may well depend on electrical properties of the char surface.

Two possible mechanisms for the deleterious effect of Na_3PO_4 treatment on decolorisation can be put forward:

i the adsorption of PO_4^{3-} ions confers a negative charge on the char surface and the effect on colorant adsorption is therefore similar to that produced by an addition of Na_2SO_4 to the liquor on

ii activating CO_2 species adsorbed at the carbon surface (as discussed previously) are displaced as carbonate ions by adsorption of phosphate ions. This can be considered as a special case of mechanism (i) above, particular to the carbon surface: the removal of the adsorbed CO_2 species as ionic carbonate also removes one of the means by which the carbon surface can acquire positive charge characteristics.

TABLE 4 Effect of exposure of Na_3PO_4 treated char to CO_2 after kilning.

	Char A Refinery kilned	Char C Na_3PO_4 treated kilned 600°/N_2	Char D Na_3PO_4 treated kilned 600°/N_2 CO_2/100°
% colour removal	75	63	78
% ash removal	10	84	74

Some evidence in support of this mechanism was provided when it was shown that CO_2 species were displaced from CAL on treatment with 30 mM Na_3PO_4; 100 μ moles/g CAL of CO_2 were released as carbonate. The Na_3PO_4 treated CAL from which CO_2 had been stripped had a lower decolorisation capacity but higher ash capacity than the original untreated stock CAL.

The adsorption isotherm of PO_4^{3-} ions on CAL is similar to that for bone char and shows that large quantities of PO_4^{3-} ions can be accommodated on a carbon surface. In fact phosphate is adsorbed very strongly for little can be removed on prolonged water washing.

The experiments with CAL leave little room for doubt that the Na_3PO_4 treatment of bone char affects some property of its carbon surface. On the basis of the proposed mechanisms, an attempt was made to reactivate a char treated with Na_3PO_4 by exposing it to carbon dioxide after kilning, following the technique which proved successful with CAL (Table 2).

Following treatment with 30 mM Na_3PO_4 a sample of Thames' fine grist stock char (Char B of Table 3) was kilned at 600°C for one hour in nitrogen. After cooling in nitrogen to 100°C the char was exposed to carbon dioxide while it cooled to room temperature.

This char (Char D) was compared with the original stock char (Char A) and the phosphate treated sample (Char C) for decolorisation and ash capacity and the results are shown in Table 4.

It can be seen that this treatment was successful in restoring the decolorisation capacity to the level of the original stock char. The ash capacity remained at an exceptionally high level.

4. Adsorption of $CaSO_4$

It has now been shown that the high temperature kilning, exposure to atmosphere and treatment with Na_3PO_4 solutions change the colour and ash adsorption properties of char in opposite directions: in the case of the Na_3PO_4 treatment, the loss of decolorisation activity is accompanied by a spectacular gain in ash removal capacity. It was, therefore, important to establish that the ash removal capacity of char could be diminished without major effect upon the decolorisation capacity.

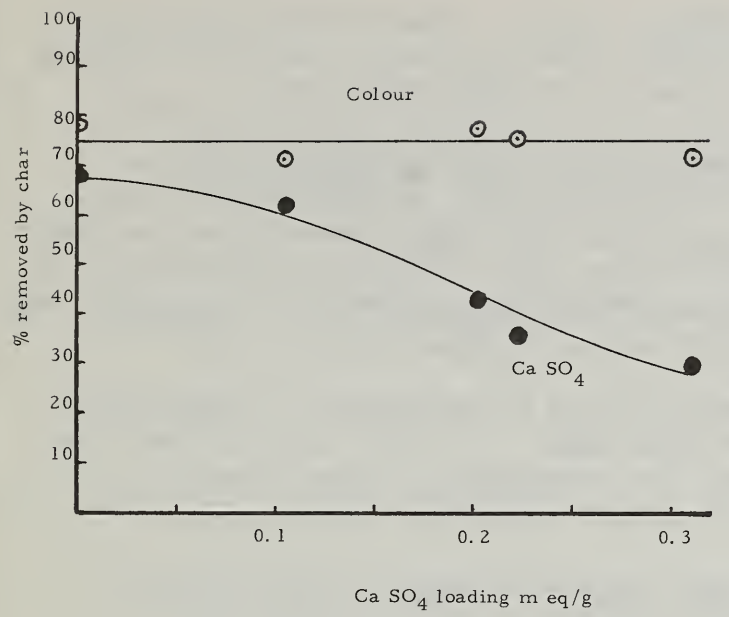


FIGURE 4. Colour and ash capacity of a char as a function of $CaSO_4$ loading.

A sample of new char was, therefore, loaded with increasing amounts of $CaSO_4$ by recycling $CaSO_4$ solutions through a column of char for increasing periods. The char was washed free from interstitial $CaSO_4$ solution with water, kilned at 400°C and the sulphate content measured. The various samples of loaded char prepared in this way were then tested for ash and colour removal capacity on a standard refinery carbonatated liquor. The % removal of colour and ash from the liquor are shown as a function of the sulphate content of the char in Figure 4.

The final sulphate loading was 50% greater than that encountered in refinery stock chars and the ash capacity was markedly reduced. The effect on decolorisation capacity is small and indicates that the adsorption of the Ca^{++}-$SO_4^{=}$ ion-pair does not occur at sites for colour adsorption.

CONCLUDING SUMMARY

These results provide the first indication that, while the apatite component certainly does adsorb a certain colorant fraction, the sites for this adsorbate differ from those for inorganic ash. In support of this it had been shown that:

i char loaded with PO_4^{3-} ions has a very greatly increased capacity for Ca^{++} and $SO_4^{=}$ ion-pairs and for ash removal from liquor, but a decreased activity for decolorisation.

ii new char loaded with a large quantity of Ca^{++} and $SO_4^{=}$ ions has a greatly reduced capacity for ash removal from liquor but an almost unchanged activity for decolorisation.

The interpretations presented in this report are generally in accordance with those of the B.C.R.P., but one or two important differences should be noted. In considering the mechanism of colour adsorption, the B.C.R.P. did not distinguish between the two types of surface but, in order to account for the

effect of the polyvalent ion balance (EPA) on liquor decolorisation, did distinguish "molecular" from "anionic" colorant. The view was taken that sulphate was in direct competition with anionic colorant for the same sites.

Electrophoretically it has been shown that the zeta potential of char particles follows the concentration of $CaCl_2$ and Na_2SO_4 in the same way that liquor decolorisation follows EPA, colour adsorption being favoured at the positive surface. It is, therefore, suggested here that the limit of the effect of EPA on decolorisation is set not by the concentration of "anionic" colorant, but by the extent of preferential adsorption of Ca^{++} or $SO_4^{=}$ ions.

In this report the evidence suggests that it is necessary to distinguish not only two types of colorant, but also two types of surface and at least two types of adsorption site. The following list summarises current views on the mechanism of colour adsorption:

(1) Two types of colorant, "anionic" and "molecular" may be distinguished by preferential adsorption on the apatite and carbon surfaces, and also by selective precipitation with TALOFLOC.

(2) Colorant adsorption is favoured at a positively charged surface which is generated by preferential adsorption of polyvalent cations and H^{+}; the effect of charge does not necessarily allow a separation of colorant types.

(3) The apatite surface adsorbs "anionic" colour and ash on different sites so that sulphate and colorant are not in competion. Phosphate ions apparently have a dominating influence on ash adsorption.

(4) The apatite surface adsorbs CO_2 to form bicarbonate ions: on contact with water or liquor some dissociation may occur and the pH decreases. The lower pH may favour colour adsorption, as indicated in (2), but it is possible that the formation of surface bicarbonate groups represents a specific chemical activation for the "anionic" colorant.

(5) The carbon surface can adsorb all colorant types but may favour the adsorption of the "molecular" species. It is likely that the use of bone char is limited by the extent and activity of its carbon surface, the first colour to leak through a char column being "molecular". On the other hand, it seems possible that the use of CAL carbon is limited by its capacity for "anionic" colorant.

(6) The carbon surface adsorbs CO_2 in the form of a bicarbonate group which does not carry its full charge. The presence of such surface groups is envisaged as causing activation of other parts of the carbon with respect to the "molecular" colorant. It is possible that the bicarbonate groups could function as sites for "anionic" colorant types but the adsorption would be very weak compared with that at bicarbonate ions in the apatite surface. In CAL carbon, of course, the latter adsorption is ruled out and it would follow that bicarbonate groups provide the only sites for "anionic" colour. On this hypothesis, the use of carbon adsorbents is likely to be critically dependent upon their reaction with CO_2.

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DISCUSSION

K. M. Bansal (Activated Carbon Div., Calgon): What is the effect of oxygen on the hydroxyapatite structure at high temperature?

J. C. Abram: Hydroxyapatite component of bone charcoal sinters when it is heated at high temperatures. This sintering reaction is accelerated by the loss of carbon which occurs when the kilning is undertaken in an oxidizing atmosphere. But the presence of oxygen does not affect the hydroxyapatite surface structure per se. This is indicated in Figures 1 and 2, which show the close relationship between the hydroxyapatite area with change in temperature and the adsorptive capacity of that surface for calcium sulphate.

K. M. Bansal: Is the deashing capacity enhanced by kilning the char at high temperature?

J. C. Abram: No, Figures 1 and 2 show that the ash capacity in fact drops at high temperatures, and this is because hydroxyapatite surface area is being lost. The amount of available surface regulates the ash capacity, and that reduced as the temperature was raised. On the other hand, the capacity for colour increased, and that was one of the main points. Apparently at high temperature in the presence of oxygen, active sites are actually put on the carbon surface and the decolorisation is enhanced. There was a loss of ash capacity, a loss of hydroxyapatite surface area which in itself can

remove some colour, but the overall effect was one of an increased colour removal activity.

F. G. Carpenter (CSSRP): You mentioned some of the effects of carbon dioxide on color removal. Would you care to mention something about the effect of carbon dioxide on the pH of liquors off char?

J. C. Abram: In general, as the exposure to carbon dioxide or air increases, the pH of the liquor off char decreases. This is why I was not able to say definitely there was an activation effect on the carbon surface after exposure to carbon dioxide. The increased decolorisation could be a pH effect, but with the CAL Carb experiment after the surface was exposed to carbon dioxide there was an increase in pH of the decolorised liquor off. We felt that indicated there was a specific activation of the carbon surface which was independent of any pH effect. But with bone charcoal, yes, as you increase the exposure to carbon dioxide so the pH of the water extract or liquor extract decreases.

F. G. Carpenter: Would not that lowering of the pH limit the amount of carbon dioxide that could be used to enhance the color removal?

J. C. Abram: I think that is true, but normally one has only a limited time between the exit of the char from the kiln and its entrance back into the next cistern so you have a self-regulating effect.

F. G. Carpenter: I appreciate that current practice does not allow enough carbon dioxide to contact the char to cause a serious pH drop. But, if you were going to take advantage of adding carbon dioxide deliberately to increase the color removal, would not the pH drop limit the amount of carbon dioxide that could be added?

J. C. Abram: I think you can stand the lowering of pH to a certain extent. Working at pH 8.3-8.4, is perhaps rather higher than absolutely necessary. I think that refiners in general are rather over-worried about the effects of low pH in liquors. It is a well-known fact that, if one heats liquor at pH 7 for long periods, there is little generation of colour and the pH remains fairly constant. If you heat liquors at higher pH's there is a generation of colour and a gradual reduction in pH which continues well below pH 7. So, I think in general we tend to run the decolorisation stations at too high a pH and lowering it by the artificial addition of carbon dioxide might give an overall benefit, provided one watches it and does not allow it to go too low, the limit depending on local refinery requirements.

F. G. Carpenter: That may be the key. You have to watch it closely. You also stated that sulfate and color were not in competition. It has been my experience that high sulfate liquors decolorize poorly over bone char. How can you reconcile that with your thought that they are not in competition?

J. C. Abram: Figure 4 indicates that there is not as much competition as people think. The composition of sugar liquors varies so much that the addition of sulfate could be masked.

F. G. Carpenter: I myself ran some experiments which were reported in the Proceedings of the 1961 Bone Char Technical Sessions [1/] in which we tried many different sulfate salts, and it was the sulfate that competed with the color not the calcium or potassium. Now maybe I did not try enough combinations, but it seemed to me at that time that there was a definite competition of sulfate and color. Now you are distinguishing two different types of colorant and finding no competition.

J. C. Abram: Yes, there do seem to be several types of colorant, and if one is only looking at the overall effect of bone char as a whole, you must bear in mind the fact that bone char contains two very different surfaces, carbon and hydroxyapatite, which each play a significant but different role in the decolorising reaction. The experiment illustrated by Figure 4 was aimed specifically at loading up the hydroxyapatite with calcium sulfate and certainly there was no reduction in the colour removal. But that could be rather different from putting calcium sulfate in the liquor.

R. K. Sinha (Calgon): You mentioned the effect of air on the carbon content of bone char. What was the temperature? How was this experiment done?

J. C. Abram: We have a steel reaction vessel into which the bone char is put and this rotates in a muffle furnace. Poking into the interior of the reaction vessel there is a steel tube through which you can pass any type of gas you like. So we can regulate the atmosphere in which the kilning is undertaken. In the first experiment we kilned the carbon in nitrogen and then cooled to about 100°C, also in nitrogen, before opening up to atmosphere. Cooling to room temperature took place in the atmosphere. In the second experiment we let it cool down in nitrogen to 100°C and then exposed it to carbon dioxide while cooling to room temperature.

R. K. Sinha: Did you try sodium phosphate treatment of exhausted CAL carbon?

J. C. Abram: If you mean CAL carbon exhausted after the treatment of impure sugar liquors, no. We treated freshly kilned CAL, exposed to air or carbon dioxide during the cooling cycle, with sodium phosphate. The resulting adsorbent was then tested for its decolorization and ash removal capacity. We found that the decolorization capacity was reduced by this phosphate treatment, but the ash capacity was enhanced. By measuring the concentration of the sodium phosphate solution after contact with the carbon, we concluded that phosphate ions were adsorbed on the surface. These ions acted as sites for calcium ash removal. We also noted that the phosphate washing resulted in the removal of carbon dioxide from the carbon surface. We attribute this loss of carbon dioxide to the loss of decolorization capacity and we believe that carbon-oxygen complexes on the surface of carbon are essential for maximizing sugar liquor decolorization.

T. N. Pearson (Imperial): When we had Peruvian raws with high sulfate, one of the tricks was to add calcium in the form of calcium chloride. This improved the decolorization by about 20%. Do you have any comment on that?

1/ Carpenter, Larry, and Deitz, Proc. 1961 Tech. Sess. Bone Char., 259-291.

J. C. Abram: I think that an excess of calcium ions in the liquor in general will increase the chance of good decolorization and ash removal, for both colour and ash adsorption on the hydroxyapatite take place as a Ca^{++}-ion pair. We think that there are two sites on hydroxyapatite surface, one for ash and one for colour. By adding calcium one is perhaps increasing the chance for colour removal on the hydroxyapatite surface without affecting the sites which are specific for ash.

M. C. Bennett (Tate and Lyle): With regard to the question of competition, when Victor Deitz and Frank Carpenter first started reporting this effect of Excess Polyvalent Anions (EPA), we at Ravensbourne got very excited about it. We felt that for the first time someone had identified one of the basic factors in the mechanism of bone char. However, we were only able to reproduce that effect in a limited number of cases. Hubert Thompson had a battery of bone char columns, and tried again and again to show that effect of EPA, but could only find it occasionally. We therefore had to go back and ask: Why did it work sometimes and not others? Why isn't the effect absolutely general? It was these questions that made Colin Abram start measuring the very properties that were supposed to change -- the electrical characteristics of the bone char surface. We started doing electrophoresis on bone char particles, because if Deitz and Carpenter were right, it had to be an electrical change, and you had to be able to pick it up in an electrophoresis cell. Well, the answer is that we found that certain bone chars were already on the limit of whatever positive charge you could generate in them, and one could therefore play about with the ions by adding calcium chloride to high sulfate liquors, and it wouldn't effect anything at all because the charge was already on its maximum. We feel that we have gone one step beyond Vic and Frank by actually measuring the basic property. This led on to what are we talking about today, sites. Is the whole of bone char the same? The point that Colin has been making this morning is that when we talk about the competition of ash, like sulfate, and of color for bone char, we are not necessarily thinking about whether bone char does a better decolorization job or not. What we have proved is that the ash and color are not in competition for the same site. The same argument applies to the effect of carbon dioxide. There we are talking about pH effects. What this paper shows is that carbon dioxide does two things. It reacts with the carbon and changes the carbon surface quite independently of what it does on the hydroxyapatite surface. Colin has shown that if you just expose bone char to air or carbon dioxide certainly the pH drops, but that by chemical juggling you can take the carbon dioxide off the hydroxyapatite surface, which puts the pH back up, and still retain the activation of the carbon surface. The whole point of this paper is to show you that the two bits of bone char can be adjusted separately and that the two components of Sugar Liquor (color and ash) can also behave quite independently of each other.

C. C. Chou (Amstar): What would be the effect of quenching the bone char in water on the performance and service life of the char in the long run? This is a common practice for activated carbon.

J. C. Abram: As far as the life and service are concerned, I do not think these would be affected, provided the temperature of the char was not excessively high. But, as for adsorption of carbon dioxide on the surface which we believe aids in the activation of the carbon surface for

decolorization, this would be reduced. So the net effect would be a reduction in its decolorization activity.

C. C. Chou: What would be the effect on the physical structure of the hydroxyapatite?

J. C. Abram: There would be no effect on the structure of the hydroxyapatite by quenching in water.

C.C. Chou: Have you analyzed the adsorption data based on the Polanyi [2/] model instead of the Langmuir model? The Polanyi model seems to be gaining popularity in the field of activated carbon.

J. C. Abram: No.

F. M. Williams (Activated Carbon Div., Calgon): Did you notice any pH effect on the effluent liquor after that excessive carbon dioxide loading on the bone char?

J. C. Abram: Yes, there was a reduction in the pH of the liquor. This is why we are not able to say positively that activation of the carbon surface was caused by the adsorption of carbon dioxide. It could have been a pH effect lowering the colour. But when the experiment was repeated with CAL carbon we obtained an increase in pH which was rather strange. That went hand in hand with an increase in decolorization performance, so we were able to put it down to the adsorption of carbon dioxide giving activation rather than a change in pH.

F. Bruder (Revere): Have you tried putting carbon dioxide into the water for quenching to see whether you would adsorb the carbon dioxide on the carbon?

J. C. Abram: No, we did not do that. That is an interesting thought. However, in water the CO_2 would convert to bicarbonate or carbonate ions. These would compete with the sulfate in ash removal so that by quenching in carbon dioxide saturated water you would probably get reduction in sulphate ash removal. But I do not think there would be any effect on the carbon surface.

J. P. Budimlya (Activated Carbon Div., Calgon): Does the result of this work alter your recommendations for normal practice in regeneration of bone char?

J. C. Abram: I think regeneration of bone char is governed by the equipment people have got. I would favour increasing the regeneration temperature to a minimum of 550°C. I think one could possibly go higher than that and get an improvement because the high temperature would favour the activation of the carbon. But then you are limited in this by the kilns and the char handling equipment which are in current use. The last thing you want to do

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2/ Polanyi, M., Adsorption and the reason for forces of adsorption. Z. Electrochem 26, 370-4 (1920).

is lose the carbon, and if you have imperfect kilning conditions, then you run the risk of losing the carbon by increasing the kilning temperature. I think that this work shows the importance of the carbon content. But one's ability to pay sufficient attention to the carbon surface is limited by present plant design.

J. P. Budimlya: Do you think it would be economically justifiable to use more fuel to operate at the higher temperatures from a performance standpoint?

J. C. Abram: There would be an improvement in activity, but at a higher cost for fuel. We have not made a commercial assessment of the situation.

M. C. Bennett: To help answer that question, I would like to refer back to the last meeting in New Orleans when we presented Part 1 of this work. We talked about high temperature activation dealing specifically with the physical changes. Someone asked whether we had applied the work in Tate & Lyle refineries, and at that time, I had to say, No, that we had not taken the risk. But now someone has taken the risk on a commercial scale. I learned about this only last night and I wonder if I could ask Mr. Van Diermen of Copersucar-Uniao dos Refinadores in Sao Paulo, Brazil, to tell you first hand of his experience. That company has taken their bone char up to very high temperatures and washed the lime out, to improve the char stock.

G. H. Van Diermen (Copersucar): We had a case of a badly treated char which was completely blocked. The carbon content had risen above 13% from the original 8%. The char had a shiny appearance. Looking at the char you could see little shiny surfaces indicating a badly blocked char. We had a choice: to throw it out and replace it by new char, or to experiment with it on the basis of the paper from Tate & Lyle given at this meeting two years ago. We tried high temperature. We raised the average temperature of the flue gas to about 600°C. Individual retort temperatures showed that the char went up to 720°C in some tubes, with other tubes ranging between 560, 580, and 590. The regenerated char was washed with hot water before sweetening on. Under these conditions, the char improved considerably. From visual observation we saw the shiny particles start to disappear. The carbon content started to drop and the activity of the char as measured in our batch test rose from 40% to 80%. It quite doubled. It was a big surprise to us.

THERMAL REGENERATION OF GRANULAR ACTIVATED CARBON

by

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INTRODUCTION

Carbonaceous adsorbents are used extensively in many applications including wastewater treatment, potable water treatment, and sugar refining. In these applications the adsorbents remove color and trace organic compounds along with some inorganic constituents.

While in use the internal pores of the adsorbent, whether it be bone char or active carbon, become filled with the adsorbed material so that the decolorizing efficiency begins to decrease. When the decolorizing efficiency decreases to a certain pre-selected level, the adsorbent is then regenerated or reactivated by thermal treatment. The regeneration process removes the adsorbed color bodies through the process of volatilization and oxidation, and the adsorbent material is then recycled for reuse.

The growing use of granular activated carbon in many industries has led to the need for improved regeneration techniques that are more energy efficient, more reliable, and with more operational flexibility. A new Fluidized Bed Regeneration System has been developed by Westvaco to meet these objectives. The design and operational characteristics of this system are discussed and compared to conventional regeneration systems.

Low temperature kilns for regenerating bone char still exist in many plants. A number of these plants could possibly benefit by replacing the bone char with granular activated carbon, particularily if the existing regeneration equipment could be used. Recent preliminary laboratory tests for one adsorption-regeneration cycle have indicated that these kilns might be suitable for regenerating granular activated carbon at the low temperatures by extending the time for regeneration. These results are also presented in this paper. Additional adsorption-regeneration cycle work is needed to determine the effect of repeated cycling on decolorizing capability.

It should be cautioned that the low temperature regeneration studies and the Westvaco Fluid Bed Regeneration System constitute two separate regeneration topics. The fact that these two advances are being discussed in the same paper does not imply that the Westvaco Fluid Bed Regenerator is a low temperature regeneration process. This is definitely not the case.

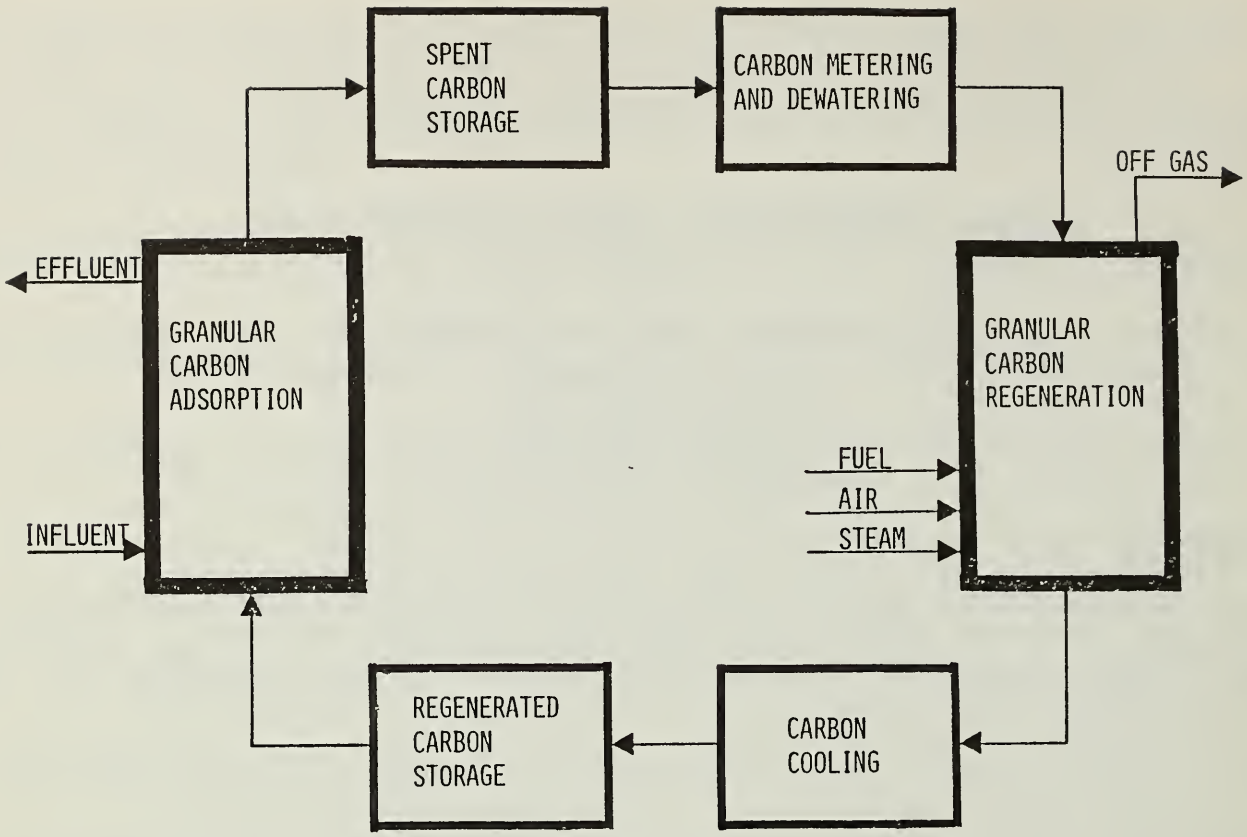

Figure 1. Use of granular carbon in sugar refining

THERMAL REGENERATION

Thermal regeneration using high temperatures and a controlled gas atmosphere is the most widely used form of regeneration for granular activated carbon although other forms such as steam stripping and the use of chemical regenerants are used in certain special applications. The role of regeneration in the use of granular carbon in cane sugar refining is illustrated in Figure 1. The influent syrup is passed through a column of granular carbon to decolorize the syrup and remove other organic and inorganic contaminants. After exhaustion, the spent carbon is removed from the adsorption column and transferred to a storage vessel for regeneration. The wet, spent carbon is metered and transferred to a dewatering screw where the moisture content of the spent carbon is reduced to about 35-50% by weight. Wet, spent carbon is fed into the regeneration system where the carbon is first dried, then pyrolized or baked, and finally regenerated or reactivated by heating to high temperatures. Fuel, air, and steam are added to the regenerator to supply the heat requirements and to provide steam for selective oxidation of the char residue. The regenerated carbon is discharged from the furnace, cooled by water quench, and transferred to a storage vessel or recharged directly to the adsorber.

A more complex description of the three stages of the regeneration process is illustrated in Figure 2. The granular carbon containing the adsorbate and 35-50% moisture is heated to about 250-300°F to dry the carbon. A majority of the adsorbate remains within the carbon pores during the drying step, although some of the more volatile organics may be vaporized off the carbon. In the

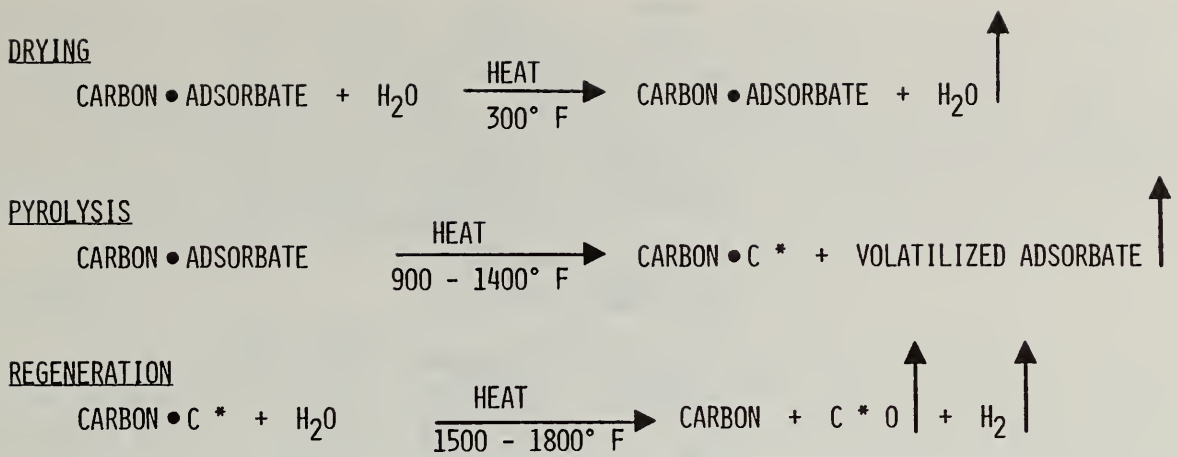

Figure 2. Process steps in regeneration of granular carbon.

second step the temperature of the carbon is increased to about 900-1400°F, where a majority of the organic compounds are removed by volatilization. Depending on the characteristics of the adsorbed material, 75 to well over 90% by weight of the adsorbate is removed during this step. That part of the adsorbate which is not removed by volatilization remains as a char residue in the pores of the activated carbon. This char residue is removed in the last and most important step of the regeneration process. This step is frequently referred to as regeneration or reactivation. The char residue is selectively removed by reaction with water vapor at temperatures of 1500-1800°F to form CO and H_2. Control of the gas composition during the pyrolysis and regeneration stages, specifically the elimination of excess oxygen, is required to minimize carbon losses during regeneration. Losses for the adsorption/regeneration system have frequently been reported as ranging from about 3-10% with 5-7% the most likely range.

EQUIPMENT FOR GRANULAR CARBON REGENERATION

Multiple-hearth furnaces and rotary kilns have traditionally been used for regeneration of granular carbon in the cane sugar area as well as other applications. As an alternative to the multiple-hearth and rotary kiln and in response to many factors, Westvaco has developed over the past five years an alternative furnace-- the Westvaco Fluidized Bed Regeneration System. The impetus for developing this system came primarily from the industrial waste and potable water areas but could certainly have application in the cane sugar refining area. The development program for the fluid bed furnace had several major objectives:

1) Reduced energy consumption
2) Improved equipment reliability
3) Production of high-quality, regenerated carbon
4) Enhanced operational flexibility with improved instrument control

More detail on the expected benefits of the fluid bed system will be given later.

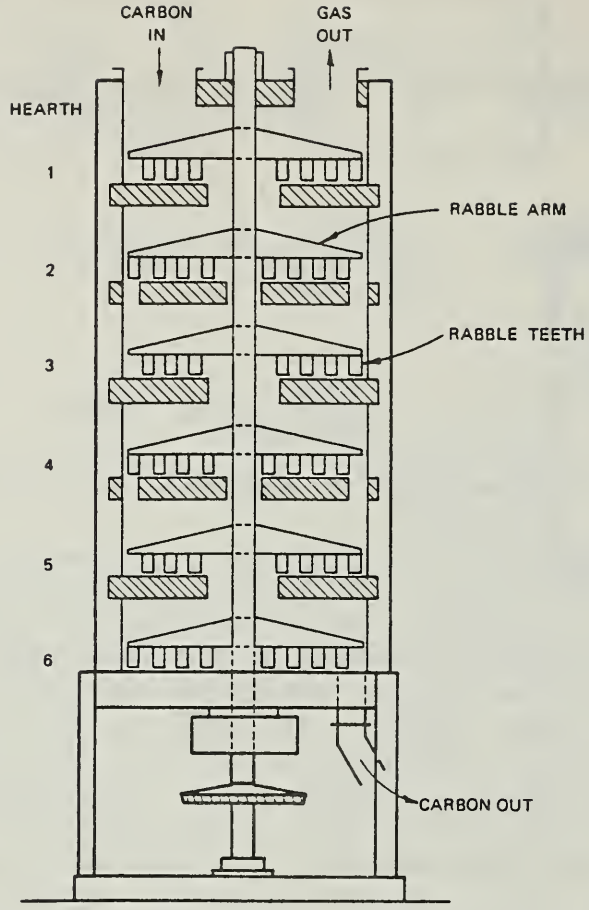

Figure 3. Cross-sectional view of multiple hearth furnace

Multiple-Hearth Furnace

Before discussing the fluid bed furnace, it would be helpful to review the multiple-hearth and rotary kilns. Large, multiple-hearth furnaces of the type shown in Figure 3 have traditionally been used for regeneration of granular carbon. This furnace consists of several self-supporting refractory hearths located one above the other contained within a cylindrical, refractory lined shell. The furnace also has a central, rotating shaft that drives rabble arms to move the carbon from hearth to hearth. The central shaft and rabble arms are hollow to allow air to flow through these parts for cooling. Wet, spent feed is introduced onto the top hearth where the carbon is dried. The carbon is then moved down to the middle hearths where the pyrolysis or baking stage is carried out. Regeneration of the carbon is performed on the bottom hearths. The heat requirements for the regeneration process are met by burning fuel in two or three burners per hearth on the bottom three hearths. Steam for removing the char residue from the pores is added through nozzles, generally on the bottom three hearths. The hot, regenerated carbon is discharged from the multiple-hearth into a quench tank. The off-gas stream from the multiple-hearth furnace normally passes through an afterburner for incineration followed by a wet scrubber prior to venting to atmosphere.

Major maintenance problems with the multiple-hearth furnace have been related to the self-supporting refractory hearths, the central shaft, and the rabble arms and teeth. The upper hearths can be easily damaged through temperature

cycling caused by feed outages or other causes. The temperature cycling will ultimately lead to the hearths assuming a negative slope followed by the hearths falling down. In some instances, the rabble arms have bent down causing damage to the hearths and central shaft. Corrosion of the rabble arms and teeth have also been problems, particularily in industrial waste treatment. Operating factors of 75-90% have been reported for multiple-hearth furnaces in the industrial waste treatment area.

Rotary Kilns

The rotary kiln is essentially a refractory lined, steel cylinder which rotates and slopes downward from feed inlet to outlet. The kiln is closed on each end by stationary hoods. In one kiln design, the heat requirements are met by a burner firing into the discharge end of the kiln. Steam is also added through this end of the kiln. The flow of combustion gases and steam is thus counter-current to the flow of carbon with the gases exhausting at 500-800°F. In most installations, these gases are passed through an afterburner to combust the organics and carbon fines. The gases from the afterburner are also passed through a wet scrubber in certain cases.

Reported disadvantages of the rotary kiln in comparison to the multiple-hearth furnace include:

1) Much larger space requirements
2) Much higher fuel consumption
3) Less control of temperatures and gas composition

Fluid Bed System

The Westvaco Fluidized Bed Regeneration System is illustrated in Figure 4. This system is a two-stage, fluidized bed process with the drying step accomplished in the upper stage and the pyrolysis and regeneration steps carried out in the lower stage. The furnace consists essentially of a refractory lined steel shell with staging provided by two stationary plates which serve to distribute the fluidizing gas and support the fluidized beds. The wet, spent carbon (35-50% H_2O) is fed from a dewatering screw into the upper drying stage. In this stage, the spent carbon is completely dried (the discharge material containing less that 1% water) by operating the fluidized bed at 250-300°F. Although not shown in this figure, the amount of heat entering the drying bed is more than the amount needed to dry the wet, spent feed. To soak up the excess heat and to provide close control of the drying stage temperature, additional water is injected into the bed. This system is also designed to maintain the bed temperature even when the wet, spent feed is completely cut off.

The dried, spent carbon flows by gravity down into the bottom, fluidized bed where the pyrolysis step is first carried out at temperatures of 900-1400°F followed by the regeneration step at temperatures of 1500-1800°F. Heat for the regeneration process is supplied by burning fuel in either one or two burners which fire into a combustion chamber which is an integral part of the furnace. The regenerated carbon discharges into a water-filled quench tank. A unique feature of the Westvaco system is the injection of air into the space above the lower fluidized bed. This air serves to burn the organic compounds

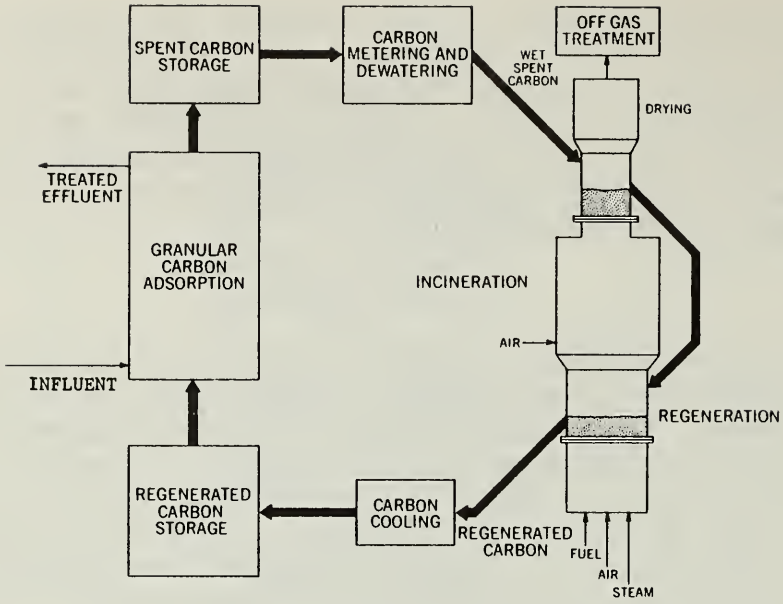

Figure 4. Westvaco Fluid Bed Regenerator in a typical adsorption system

volatilized from the carbon in addition to the H_2 and CO formed by the oxidation reaction. Part of the heat derived in this zone is radiated down to the regeneration fluidized bed with the remainder serving to provide the heat needed to dry the carbon. Incineration in this manner can serve in many applications to eliminate the requirement for an external afterburner, with the off-gas treatment system consisting only of a wet scrubber to remove carbon fines.

The First Westvaco Fluid Bed System

The first Westvaco fluid bed system was installed in a wastewater treatment application at a Hercules plant in Hattiesburg, Mississippi. This Hercules plant is a diversified organics production facility and has a complex wastewater stream. The fluid bed system was selected by Hercules as a replacement for a multihearth furnace which had experienced numerous mechanical problems and significant downtime. The fluid bed unit was started up in late July of this year at which time the multihearth furnace was shut down. The Fluid Bed has performed according to design specifications, and the system has been demonstrated to have the capacity for processing up to 40,000 lbs/day of spent feed while producing a high quality, regenerated carbon. In this application, the regenerated carbon has consistently maintained an efficiency of 110-120% compared to virgin carbon and using TOC removal as an indicator. The first few months' operation of this unit has certainly indicated that this system is a viable alternative to the conventional equipment. Detailed operating data on this Westvaco Fluid Bed System is expected to be available in the near future.

Design and Operating Benefits

In comparison to the multiple-hearth furnace and rotary kiln, the Westvaco Fluid Bed Regeneration System offers a number of benefits.

1) Improved Fuel Economy

The fluid bed furnace requires only about 1700 BTU/lb regenerated carbon versus reported values of about 2500-8000 BTU/lb for the conventional equipment. These values are for the regeneration furnace only and do not include any afterburner fuel. Another 3000-9000 BTU/lb carbon is normally required for the afterburner for the conventional furnaces, while the fluid bed furnace will not require an afterburner in many applications.

The economy of the fluid bed furnace is related to:

a) improved heat and mass transfer rates due to the intimate contact between the gas and solid. The higher heat and mass transfer rates result in a throughput of 1000-2000 lb/day sq ft of gas distribution plate area as compared to about 50-100 lb/day sq ft of hearth area for a multiple hearth furnace.

b) absence of moving parts in the high temperature zone that require cooling air.

c) lower off-gas temperatures from the drying section, since the gas is in equilibrium with the carbon bed.

d) recovery of heat from the incineration zone.

2) Lower Maintenance Requirements

The fluid bed does not contain any self-supporting refractory hearths or internal moving parts in the high temperature zone to break down. Absence of the self-supporting hearths means that the fluid bed unit is not as susceptible to temperature variations and feed outages. Even if a problem should occur with the only internals, the grid plates, the furnace is designed with flanges for quick disassembly, installation of a new plate, and reassembly.

3) Uniform, High Quality Product

The furnace can be designed to provide close automatic control over the fluidizing gas composition and the drying and regeneration stage temperatures. Instrumentation is supplied to automatically monitor and maintain zero excess oxygen in the gas contacting the lower fluidized bed. The furnace design can also provide provisions for carbon fines removal to eliminate possible pressure drop problems in the adsorption columns.

4) Quick Start-Up and Shutdown

Absence of the self-supporting, refractory hearths means that the fluid bed unit does not have to follow a rigid schedule for heat-up and cool-down. It has been demonstrated in pilot and plant facilities that only 2-4 hours are required for start-up beginning with a cold furnace.

6) Operational Flexibility

The ability for quick start-up and shutdown allows the system to operate with considerations given to manpower availability and operating schedules. Due to the rapid response time and relatively short carbon residence times

characteristic of a fluidized bed, changes in operating conditions can be easily made with rapid response of the regenerated carbon.

Design Program

Westvaco has developed a thorough test program to provide design and operating information for the fluid bed regeneration systems. The first step in this program utilizes a bench scale fluidized bed unit to determine the feasibility of regenerating spent carbon from a particular application and to develop information on the effect of various operating parameters on the quality of the regenerated carbon. The type of information developed from this unit is illustrated in Figures 5, 6, and 7 for a spent carbon sample taken from a cane sugar refinery.

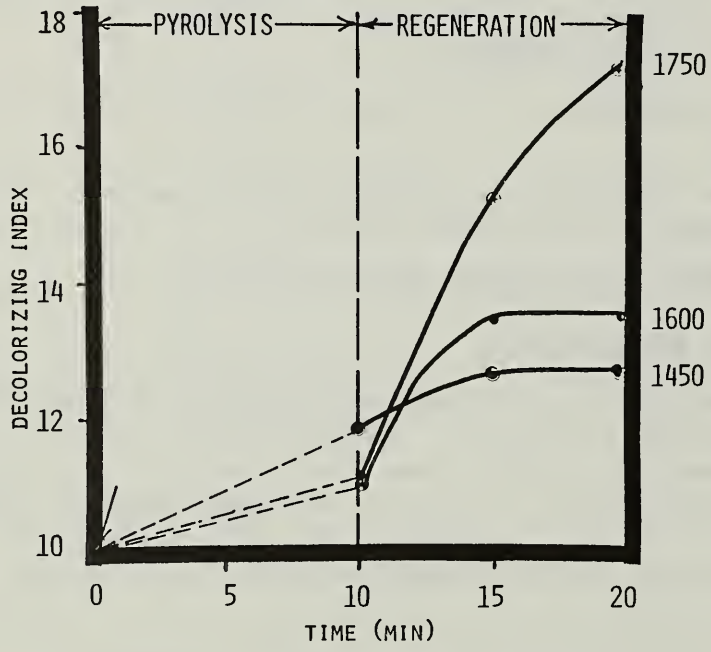

Figure 5. Fluid bed regeneration of spent carbon from cane sugar processing

Figure 5 shows the effect of temperature and residence time on development of the molasses decolorizing index. Over the first few minutes, 10 in this case, the carbon is pyrolized or baked as the carbon heats up to the regeneration temperature. During this period the decolorizing index increased from the spent carbon level, 10 to between 11 and 12 depending on the temperature. At temperature levels of 1450 and 1600°F, the decolorizing index increased over the first five minutes of regeneration but showed no increase for longer times. This would seem to be an indication that the more reactive char residue was removed during this time period, at least from the pores of a size that is correlated with decolorizing index. Reaction of the base carbon was insignificant at these temperature levels.

At the higher temperature of 1750°F, the D.I. increased with time as might be expected, since this temperature is in the range normally used for activation of virgin carbon. Analysis of 15 samples of the plant regenerated carbon about this same time period showed an average decolorizing index of 10.2. With this information as a basis for comparison, the bench scale

test work would certainly seem to show that the fluidized bed technique can regenerate carbon from cane sugar refining.

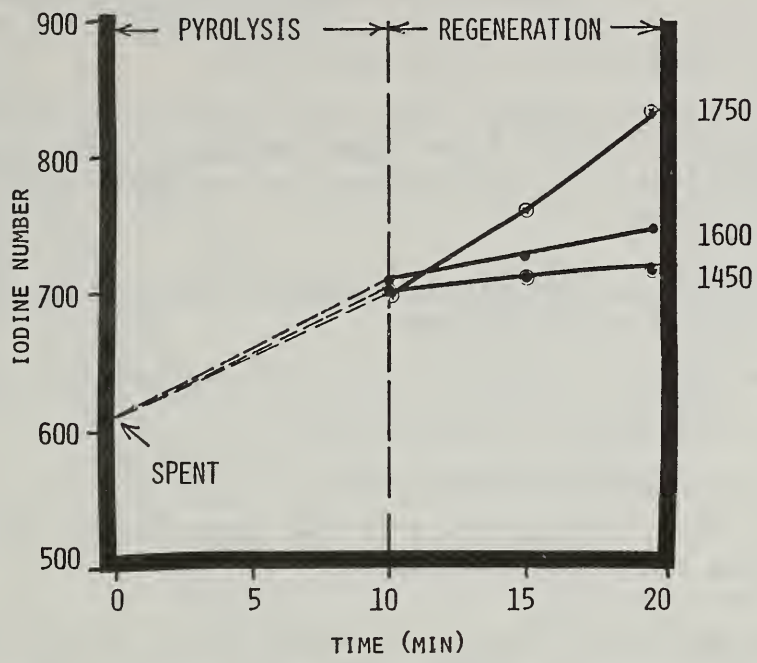

Figure 6. Fluid bed regeneration of spent carbon from cane sugar processing

The development of I.N. is shown in Figure 6. Starting from slightly over 600 for the spent carbon, the iodine number increased to about 700 during the pyrolysis stage and then increased to between 700 and 800 during regeneration, depending on the temperature level. Analyses on 9 plant regenerated samples from about the same time period showed an average iodine number of only about 664.

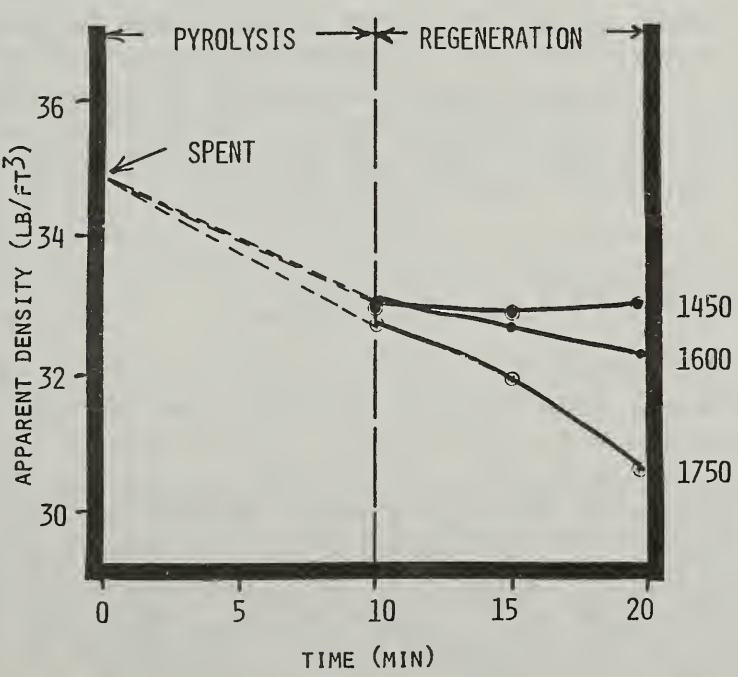

Figure 7. Fluid bed regeneration of spent carbon from cane sugar processing

And finally, the change in apparent density is shown in Figure 7. The density decreased from about 35 lb/ft^3 for the spent carbon to 33 lb/ft^3 during pyrolysis. There was an insignificant change in density with regeneration at 1450°F which agrees with the iodine number results. The density decreased with time during regeneration at 1600 and 1750°F.

In summary, these results indicate that the fluid bed is a viable technique for regenerating carbon used in cane sugar refining. The results also give an indication of the type of information developed that goes into the design of a plant system.

In addition to the results presented, other information developed in bench scale tests or analyses would include:

1) Complete characterization of the spent and regenerated carbons.
2) Information on materials of construction.
3) Information on off-gas treatment needs.
4) Information on trace contaminants in the spent carbon that might affect operation of the fluidized bed unit.

Westvaco also has available a large commercial scale facility that has the capacity to process tonnage quantities of spent carbon. When large quantities of spent carbon are available, complete design and operating information can be developed through a several day test run.

With a test program of this type and with the equipment available, sufficent information can be developed to produce a viable fluid bed regeneration system.

LOW TEMPERATURE REGENERATION

As previously mentioned, granular carbon regeneration is normally accomplished at 1500-1800°F to restore most of the activity parameters to their virgin values However, in the sugar industry where the removal of large color bodies is the major goal, there may be some flexibility in regeneration conditions. Here, carbon performance is dependent upon the existence of large pores as indicated by the molasses decolorizing index, and the iodine number is less significant. This provides some operational flexibility since the decolorizing index may be restored or increased at the expense of decreasing the iodine number. This is not a feasible alternative in many areas.

If granular activated carbon can be regenerated in bone char furnaces, this would provide cane sugar processors additional flexibility in their operations. The regeneration requirements for granular carbon depend upon the nature of the adsorbate, the characteristics of the carbon, and the organic loading achieved. The influence of these parameters was demonstrated by Hemphill(1) and are shown in Figure 8 for methylene blue. It should be noted that the ratio of the adsorptive capacity of the regenerated carbon and virgin carbon is a linear function of the regeneration temperature and adsorbate loading. This suggests two important points. The first is that the regeneration rate is almost independent of sorbate loadings at high temperatures. Second, it presents the possibility that the lower rates may be partially

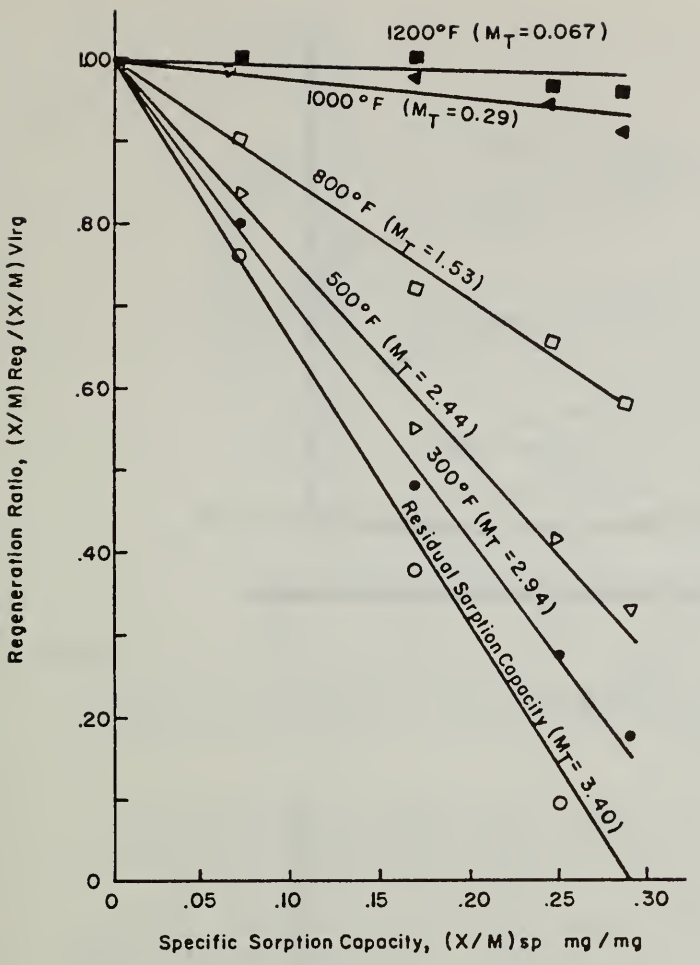

Figure 8. Effect of specific sorption capacity and temperature on regeneration efficiency (Hemphill)

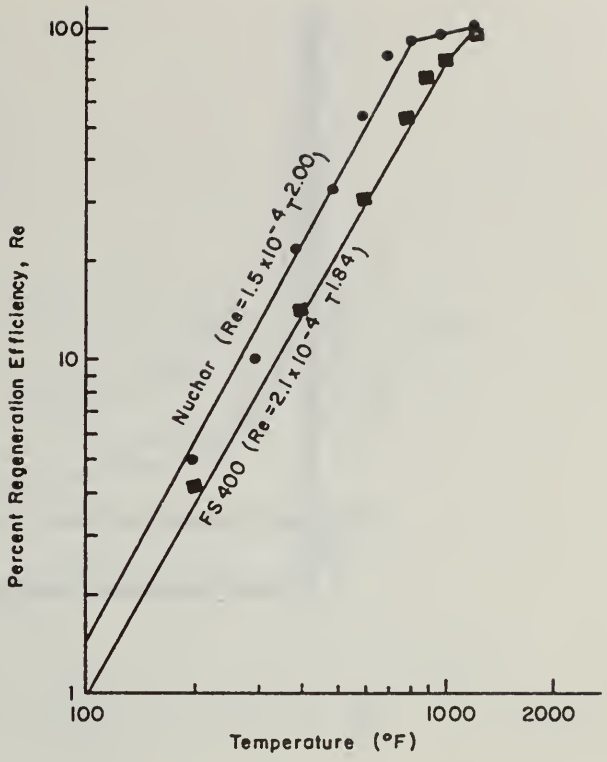

Figure 9. The influence of time on the regeneration efficiency for petrochemical waste carbons (Hemphill)

compensated for by increasing the time of regeneration. This could be significant in the sugar industry where the granular carbon use would be about 10% of the bone char usage rate and large, low temperature bone char regeneration furnaces are already in place.

The influence of temperature on regeneration efficiency is also shown in Figure 9 for a petrochemical waste carbon which was totally regenerated at 1000°F. The regeneration times were essentially constant at 2.5-3.0 hours, so it is interesting to speculate as to shifts in the inflection point at various times.

To examine the time-temperature relations required for carbons exhausted in cane sugar processing an adsorption and regeneration study was conducted. To obtain exhaustion at minimum syrup throughputs a Suchar 681 sample was selected which just met the minimum iodine number and decolorizing index specifications. A 2000 gram portion of carbon was placed into 4" diameter adsorption columns and washed sugar liquor applied at a rate of 0.11 gpm/ft^2. When the carbon was exhausted at these conditions, a remelt sugar was applied under these same conditions until total exhaustion

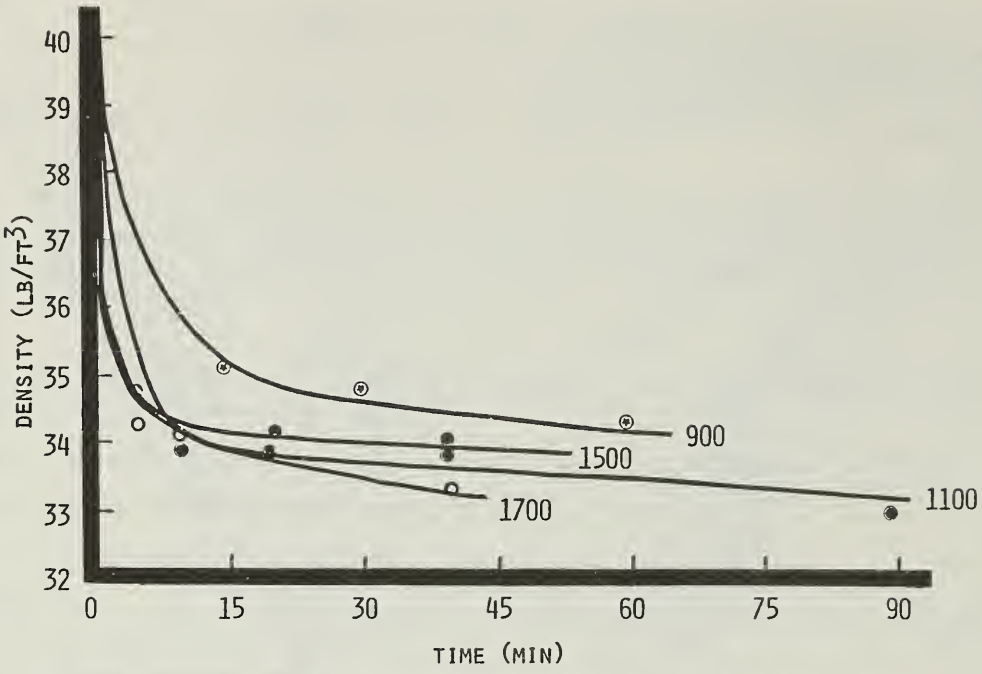

Figure 10. The influence of time and temperature on the density of Suchar 681 from cane sugar processing

occurred. The carbon was then washed with seven bed volumes of tap water and drained. The carbon was removed from the columns, mixed and divided into five portions. One portion was analyzed to determine the quality of the spent carbon, while the others were regenerated at 900, 1100, 1500, and 1700°F respectively at various times. The virgin, spent and regenerated carbons were analyzed for apparent density, iodine number, decolorizing index, volatiles; and, the abrasion number was run on selected samples. The initial results of this study are shown in Figure 10. At all four regeneration conditions the apparent density was decreased from the 40.6 lb/ft^3 value for the spent carbon to a value near the 34 lb/ft^3 value of the virgin carbon. The sample regenerated at 900°F was the only material that was not brought back to an apparent density of 34 lb/ft^3 or lower.

The influence of time and temperature on the iodine number and decolorizing index are shown in Figures 11 and 12. It is obvious that the iodine number restoration is highly influenced by the regeneration temperature. The highest iodine number achieved at 900°F was 865 or 80% of the virgin carbon. At 1700°F iodine numbers of 1033 were obtained compared to 1086 for the virgin carbon. Based on iodine numbers reasonably efficient regeneration is being achieved at both 900 and 1600°F. The decolorizing index (D.I.) was not restored to the desired level, even at 1500 and 1750°F. Obviously the optimum conditions had not been achieved during this first trial run. Even at 900° the D.I. was restored from the 5.5 value of the spent carbon to 7.2 or 90% of the original D.I. of 8.0. This is still not as efficient as expected at high temperatures and reinforces the earlier observation that optimum gas composition had not been achieved. Typically, the decolorizing index can be restored to values above that of the virgin carbon as shown in Figure 13. This is based on work by Smith et al (2).

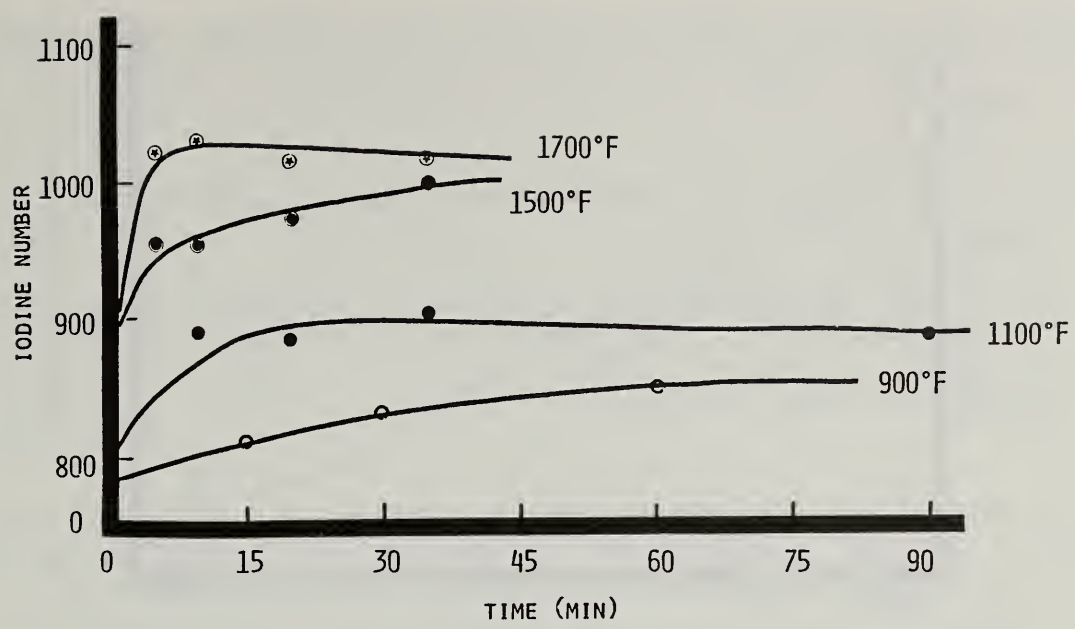

Figure 11. The influence of time and temperature on the iodine number of Suchar 681 from cane sugar processing

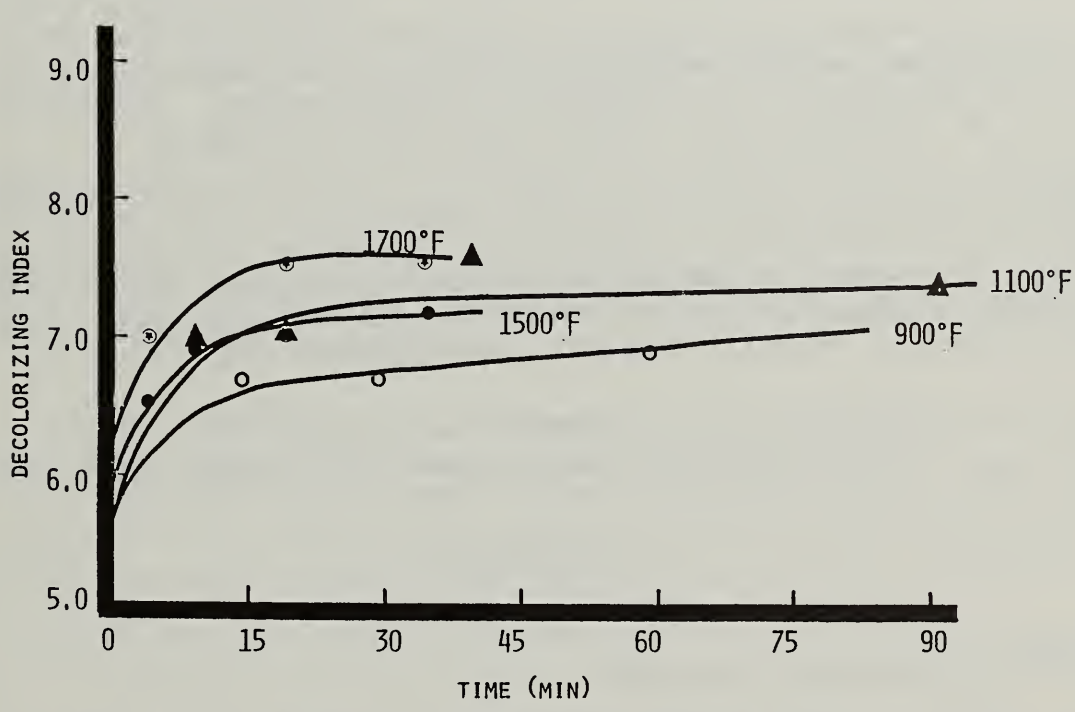

Figure 12. The influence of time and temperature on the decolorizing index of Suchar 681 from cane sugar processing

While these data are by no means conclusive, they suggest that low temperature regeneration may be technically feasible. The studies are being repeated and cyclic studies undertaken to ascertain the long term effects.

SUMMARY

The Westvaco Fluid Bed Regeneration System is a significant advancement in granular carbon regeneration and should contribute to the economical

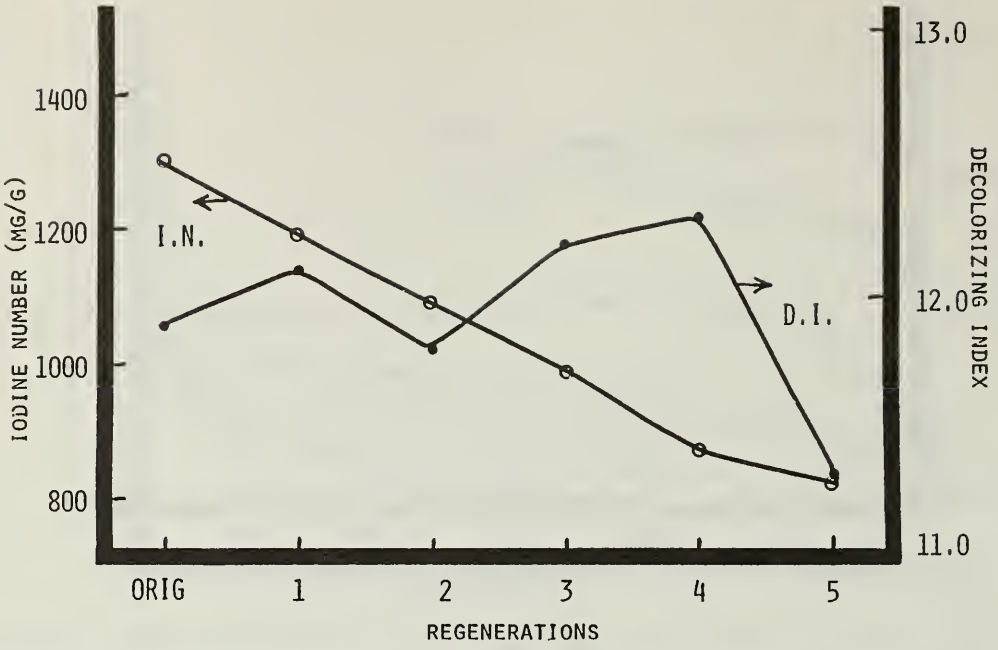

Figure 13. Properties of original and regenerated Suchar 681

operation of cane sugar processors. In addition, low temperature regeneration in bone char furnaces appears to offer a technically feasible basis for cane processors to use granular activated carbon. While more work needs to be completed, the initial data look encouraging.

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1) Hemphill, L., Thermal regeneration of activated carbon, Project Report S800554, Robert S. Kerr Environmental Research Laboratory, U.S. Environmental Protection Agency, Ada, Oklahoma (May 1978).

2) Smith, S. B.; Laughlin, H. F.; Formeck, C. G. and Walters, C. O., Refinery testing of an improved granular carbon, Proc. 1970 Tech. Sess. Cane Sugar Refining Research, Boston, Mass. (October 12-13, 1970).

DISCUSSION

K. M. Bansal (Calgon): What is the reduction in mean particle diameter in the fluidized bed regeneration process?

B. H. Kornegay: There is less change in a fluid bed than in a multi-health furnace.

K. M. Bansal: How much fines (below -60 mesh) are generated in a fluid bed as compared with a multihearth furnace?

B. H. Kornegay: The minus 60 mesh fines are the total losses in the fluid bed and have been measured at 1% to 3%.

K. M. Bansal: What is the atmosphere that you used for the low temperature regeneration? Did it have oxygen or steam?

B. H. Kornegay: The atmosphere had steam and a slight residule of oxygen. We determined the loading of these spent carbons after regeneration using a cane syrup, and found they varied from 85 to 116% of the virgin carbon as we went from 900 to 1750°F.

R. K. Sinha (Calgon): What is the highest temperature you can go to in the fluid bed unit?

B. H. Kornegay: The structural limitations are the same as those for a multi-hearth kiln. You are still limited to about 2000°F (1100°C).

C. C. Chou (Amstar): Would you be able to regenerate carbon with about 30% filter aid in it?

B. H. Kornegay: The filter aid would produce a problem. In fact, in an installation at Hercules, they had sand in their system. The way we handled that was to put a sand table in front of the regeneration equipment to remove the fine sand. So the most productive way to get around filter aid would be to put in a separation system. This is a granular regeneration process and not intended for powders, so you could separate fine material from the granular with a sand table. With the powdered carbon operation we would use the transport system.

C. C. Chou: I understand you also have a fluidized bed for regenerating powdered carbon.

B. H. Kornegay: Right. We call it the transport reactor system. Basically it is a process in which the powdered carbon enters near the bottom of the reactor and the heat and expanding vapor causes the particles to move upward. So the carbon is never retained in a bed but is moving through the furnace. The residence times are a few seconds. In the granular carbon fluid bed system the residence time is measured in minutes.

C. C. Chou: For the low temperature regeneration, how long did you wash the carbon before it was taken out of the cistern for kilning?

B. H. Kornegay: We did not wash it as much as you would in a refinery because we wanted to put as many volatiles in the furnace as possible. We put seven bed volumes of water through the carbon for washing.

C. C. Chou: According to your bulk density data the carbon seems to absorb at least 15% of organic matter. I expect most of it will be sucrose. In the refinery we don't have much sucrose left on the carbon. The Bone Char Project had the figure of 0.4% sucrose remaining on bone char, with somewhat more on granular carbon, if I remember correctly. So if the carbon is washed thoroughly, there will be little difference in bulk density between the regenerated and spent carbon. If you do that thorough washing before the drying and regeneration, you may be able to regenerate at lower temperature, without a lot of difference in the results such as between 1100 and 1500 iodine number.

B. H. Kornegay: Yes, the pick-up here was about 18%.

F. G. Carpenter (CSRRP): Granular carbons retain about 10 times more sucrose than bone char, or a few percent.[1/]

Your spent carbon has been given an extremely unusual loading. After your liquor cycles, you did not really wash it enough, so you did not have what would be a typical spent carbon. Of the 18% organics that were loaded on the carbon, at least 10% or 12% were sucrose. Nobody would throw away that much sucrose even though they were burning only 1% carbon on melt.

I might add that if the carbon (or bone char) is heavily loaded with color bodies or organic non-sugars, there will be less sucrose in the part that can not be washed off.

F. M. Williams (Calgon): I would like to take issue with Carpenter in regard to that 10% to 12% sucrose loss on carbon. I have had sugar refiners test carbon after a good sweetening off operation and the figure is 5% to 6%. I don't want those higher figures to scare anyone away from putting granular carbon on stream.

C. C. Chou: We found out that after a thorough washing of activated carbon you would have about 2% sucrose left on the carbon.

G. H. Van Diermen (Copersucar): What is the pH of liquors off the granular carbon that is regenerated at low temperatures as compared with granular carbon that is regenerated at high temperatures?

B. H. Kornegay: We have only looked at pH in the single cycle data and of course granular carbons used in cane sugar decolorization such as Suchar 681 have a pH control additive. We found no pH difference between the virgin and the once regenerated material.

J. P. Budimlya (Calgon): We are all interested in the economics of the equipment part. The Herreshoff Furnace is obviously a very expensive part of a granular carbon system. Could you comment on the capital cost savings of your system.

B. H. Kornegay: We have bid against all kinds of other furnaces: the Herreshoff, the Rotary, other fluid beds, and the infrared. It would appear that that we are talking about something on the order of 20% to 30% less than the other systems. This is for both fixed cost and operating cost. It is certainly better than 10%.

F. M. Williams: You gave an energy figure of 2000 to 2500 BTU per pound (1100 to 1400 Kcal/kg) of carbon. Does this include the energy necessary to spend in an afterburner to burn off the noxious gasses?

B. H. Kornegay: That includes the after-burner, which in our system is between the regeneration plate and the drying plate. The energy for the after-burner is included in other systems with which we made comparisons.

1/ Carpenter, F. G., Proc. Tech. Sess. Bone Char 1957, 279-296.

THE WORLD SUGAR RESEARCH ORGANIZATION

by
Stephanie S. Hillebrand[1/]

The idea of a U.S. organization devoted to cooperative sugar research was conceived in 1943 by the late Ody Lamborn, who translated his idea into the Sugar Research Foundation, located in New York City. In reviewing the list of industrial sponsors of the Cane Sugar Refining Research Project, Inc., I note that some of this organization's patrons were also charter members of the Sugar Research Foundation. In 1968, the Sugar Research Foundation, hereafter, S.R.F., expanded its horizons to include members from Belgium, Ireland, England, Australia... and added the prefix "International" to its title. This International Sugar Research Foundation then moved to Bethesda, Maryland so that it would have access to the research facilities of the National Library of Medicine and the National Institutes of Health. The "ISRF" devoted itself to continuing the work of the domestic group which had established a sound research program focussed on three aspects of sugar utilization: Sucrochemistry, Food Technology and Public Health. The World Sugar Research Organisation, which succeded the ISRF this year, will continue to monitor developments, promote research, coordinate activities and disseminate information in these areas.

You may be wondering why Sucrochemistry, Food Technology and Public Health?

The study of sucrose as a chemical raw material, or "Sucrochemistry" evolved from the combined realization that sucrose is the most widely produced, regenerable, and usually the cheapest, pure, organic chemical in the world, and that the world's reserves of fossil fuel are limited. Sucrochemistry is beginning to produce results. To give just one example, Brazil is the leader today in conversion of sugar to alcohol but other countries will surely follow.

With the population of the world exploding, the efficiency of food production per resource input becomes a very important issue.

Production of sugar is the most efficient means of focusing solar energy in the world. Sugarcane is 400% more efficient, in terms of harvestible dry matter per hectare, than any other dry tropical plant, and sugar beet 200% as efficient as any other temperate zone plant. It takes 7% of a hectare to produce one million kilocalories in the form of sugar; 7.7 hectares is required to produce the same energy in the form of beef -- 110 times as much land. It is therefore obvious that world demands for edible energy will require the growing and production of sugar.

It is as an edible substance that sugar has found itself in a lot of hot water.

Food technology, the second area of research, is the response to several factors: more women going out to work, a decrease in the amount of food prepared in the home, and an increase in the demand for manufactured convenience foods.

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Health related research, the third area, is more complicated. As energy requirements by the individual living in industrially developed countries have been reduced by the wide spread use of mechanical transport and aids to living, by increasing use of central heating and by passive recreation, there has been another form of population explosion, which in this case is related to the waistline. Creeping overweight has been fueled by the success of medical science in finding single causal factors and cures for most infectious diseases, and therefore having more of us live longer to do battle, in our fatty armour, with such multi-factoral diseases of old age as heart attacks, cancer, strokes and diabetes.

Because sugar is present in so many foods, it is an easy target and a number of self styled experts would link these diseases, and a grocery list of others, to sugar. At the same time, but because of the high cost of national health care, governments and other agencies in many countries have become increasingly interested in diet and health, publishing reports on heart disease, obesity, diabetes and dental caries, and sometimes postulating a connection between diet, particularly sugar and the incidence of these conditions. The McGovern Committee report is a striking example.

Debate and controversy are essential if the truth is ever to be known, and although thousands of scientific papers are published every year, the medical aspects of sugar and health are still very confused. Nobody knows even the true range of intakes of sugar. Nobody knows what is "too much" sugar, or what nutrients may or may not be displaced at various levels of sugar intake, or with what effect or how it may vary for individuals. Nobody knows if sugar is more "fattening" that other carbohydrates, or different components of diet, as is sometimes suggested. Comparatively little is known about "carbohydrate sensitivity." It is known, however, that the public is subjected to, and all too often succumbs to, a vast array of misinformation and food faddism, which is not entirely favorable to sugar. Remedial action is called for.

The sugar industry has always recognized its responsibility for providing a safe, versatile and reliable food and sweetener. It is not necessary for those who are involved in the industry to know more about the role of sugar in diet and health. Individual sugar companies cannot by themselves afford to undertake to find all the answers, and even if they could, their statements would be viewed by many as self serving. A good deal of non-industrially supported research is being carried out, often with resources provided by government and independent foundations, but the situation regarding this varies widely from country to country. A means of collecting and disseminating current scientific information regarding sugar and a means of continuous contact between the sugar industries of different countries is therefore needed.

It is to answer this need that the World Sugar Research Organization succeeded the I.S.R.F. with the support of the sugar industries from: Belgium, Canada, Ireland, South Africa, the U.K., the U.S. and Venezuela.

The objectives of the W.S.R.O. are:

(1) The monitoring and collection of information on research work done in different regions. This can partly be accomplished by means of helpful con-

tacts in the countries and partly by the use of such a service as the British Library Automatic Information Service, which provides access to data banks throughout the world.

For those of you who may have found the I.S.R.F a convenient source of information, I am pleased to mention that the reports of the 380 ISRF research projects and the entire subject files were shipped to the London office of the WSRO. where they will again be available for general use.

(2) The diffusion between regions of this information to those who make decisions in the industry and to those who advise them.

(3) The provision of a meeting ground for executives and scientists to discuss matters of common interest relating to research.

(4) The maintenance, and where necessary establishment, of contacts with those doing research.

(5) The identification of gaps in research effort and the stimulation of studies where this is needed.

(6) The assesment of the potential effect of the researches being done or contemplated on the position of sugar as a major item of human diet and as a possible basis for other uses.

The organization will depend on the work of Regional Research Advisory Committees. It does not duplicate research work, and will only sponsor it when there is a gap which all concerned recognize as a suitable object for sponsorship. Members will however sponsor research, either regionally or individually, in such a way as to meet their own requirements and the information will be available to all.

It is in this last respect that the WSRO differs mainly from the ISRF.

The Directors of the WSRO had their second meeting in mid-September, 1978 in Washington, D.D.: Areas of research which were considered of general interest include dental caries, heart disease, overweight.

The next meeting of WSRO members will be Caracas, Venezuela in March of 1979. The occasion will also feature a symposium on health related issues.

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DISCUSSION

F. G. Carpenter (CSRRP): We have here today people who are interested in processing sugar as well as selling the finished product. There is also another

big group interested in the growing of the crop. Can we make it clear what part the WSRO plays? Do you do any research in sugar production? New sugar producing plants? Do you do any research in processing or any of the problems before you get to the final white sugar? Or do you work only in the white sugar and what you can do with it?

S. S. Hillebrand: The WSRO is concerned with the utilization of refined sugar and sugar by-products. Currently, a major effort is being directed toward establishing the safety of sugar as an ingredient in a balanced diet.

J. F. Dowling (Refined Syrups): Is your group doing any further work on sweetness and taste profile or body? HFCS is coming along and many of the claims about higher sweetness are questionable. We sell sweetness and body.

S. S. Hillebrand: There has been some discussion about investigating the relative merits of various sweeteners, but at the moment the WSRO is sticking strictly to sucrose. It is recognized, however, that sucrose is becoming more involved in a "sweetener" situation.

M. C. Bennett (Tate & Lyle): Do people pay a subscription to become members of your organization? And having received such subscriptions do you then sponsor research projects in Laboratories or Research organizations? In which case, how do you select projects?

S. S. Hillebrand: Dues are levied and the amount varies with the different categories of memberships. The dues are quite low, and they are used for administration and coordination. The sponsorship of research projects is left to the members. WSRO does not sponsor projects except in the instance where all members recognize that a project needs to be done, and the magnitude is such that no one region or several regions combined could do it, in which case all regions together (which is WSRO) may elect to do it. This system evolved from a problem with the ISRF, which gathered dues to fund a general research package. There was such a diversity of interests and needs that the regions were not satisfied that they were getting what they wanted. So, in WSRO, each region can do what it wants, and WSRO disseminates the results. WSRO also ensures that the research capabilities in various countries are made available to all members. WSRO is not a central office using everybody's money to do what some may not wish to have done.

M. C. Bennett: Does the WSRO itself join other organizations? For instance, would you be interested in joining our organization?

S. S. Hillebrand: I don't think that has been considered. Would you like to join ours?

M. C. Bennett: I think we could make a deal on that.

S. S. Hillebrand: I think there should be some cooperation; I see several of our members are also members of CSRRP. Perhaps a mechanism for exchanging current information could be developed which would be useful for everyone.

THE EVALUATION OF ION EXCHANGE RESINS FOR SUGAR DECOLORIZATION

William Fries and R. W. Walker

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ABSTRACT

The study of ion exchange resins for the removal of color from cane syrups requires special techniques and hardware. The problems of laboratory column dimensions, the parameters important to ion exchange resin decolorization and the necessity of multicycling data are discussed. Optimum resin systems are shown.

INTRODUCTION

Synthetic ion exchange resins have been accepted as integral parts of refineries for the removal of color. Usually, the position of use is after a clarification-filtration step and possibly after additional pretreatments such as bonechar or granulated carbon. The major problem with testing ion exchange resins in these applications is that a significant change in decolorization occurs after several years of use. Many changes can be ascribed to variations in conditions and sugar sources. However, the progressive fouling and other chemical changes occurring within the resin can cause systematic losses in decolorization efficiency.

AUTOMATIC CYCLING EQUIPMENT

A device has been developed in our laboratory which automatically and accurately cycles an ion exchange decolorization bed through the various steps and does this repeatedly for as many cycles as required to give reliable results. No acceleration of life testing is attempted with this apparatus. Its main advantage is its ability to operate continuously 168 hours a week with little maintenance-5 to 10 hours a week excluding analytical time. This cycler consists of the column assembly containing the resin, very precise and reliable pumps (Milton Roy Co.), fluid transmission lines and electrically operated solenoid valves. The pumps are constant displacement and work against 60 psi spring loaded ball valves to ensure constant flow. Flow is easily adjustable at the pump and has shown consistency over months of operation within 2% accuracy. The apparatus is shown in Figures 1 and 2.

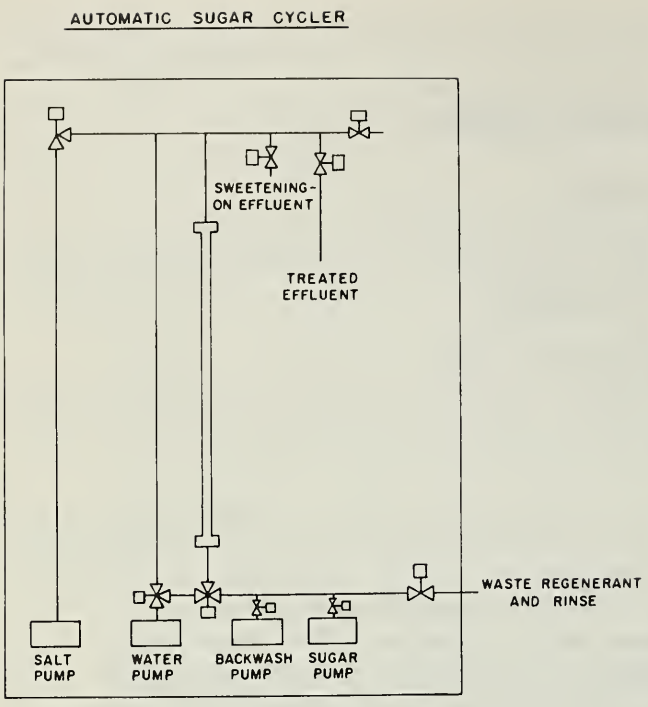


FIGURE I

Schematic of Automatic Sugar Cycler

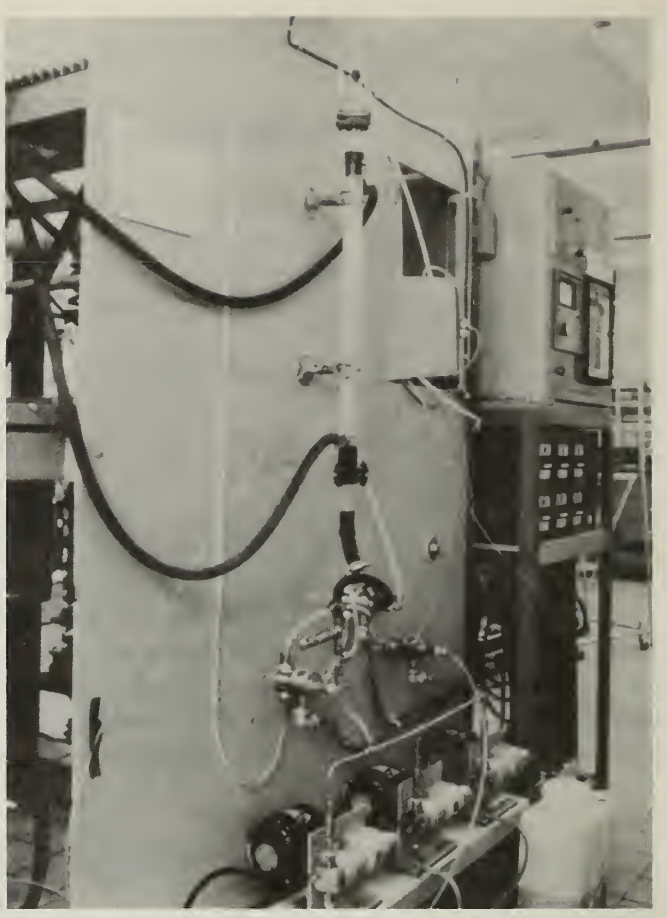


FIGURE II

Automatic Sugar Cycler

Controlling all of this is a digital programmer which controls the solenoid valves and pumps. The programmer consists of mechanical cams which activate toggle switches for each electrically operated component in the predetermined sequence. The programmer is flexible in that the time of any phase of the cycle can be changed with the push of a button and the direction of the regeneration can be either concurrent to decolorization flow or countercurrent. There is capacity for six separate functions which are usually

1. Sweetening On - Effluent is discarded.
2. Decolorization - Effluent is collected and analyzed for color.
3. Sweetening Off - Effluent is collected with 2.
4. Backwash - Effluent is discarded.
5. Regeneration - Effluent is collected and analyzed for color.
6. Rinse - Effluent is collected with 5.

Photographs of the programmer are presented in Figures III and IV.

The effluent color is monitored periodically using the ICUMSA (420 mμ) method. The syrup from local refineries was introduced to the

FIGURE III

Programmer
(Front View)

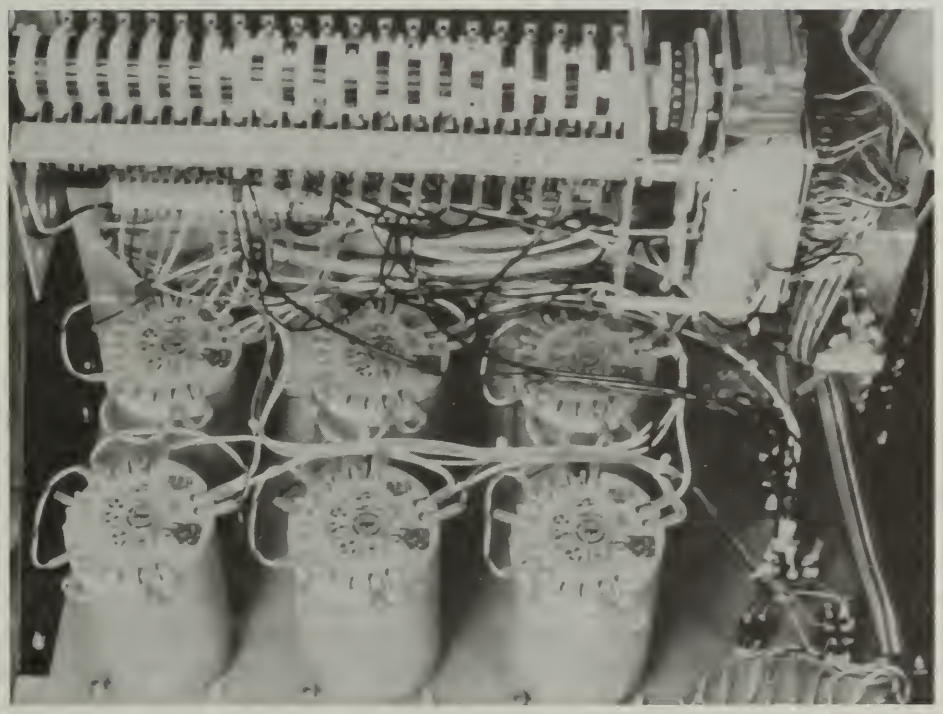


FIGURE IV

Programmer
(Inside)

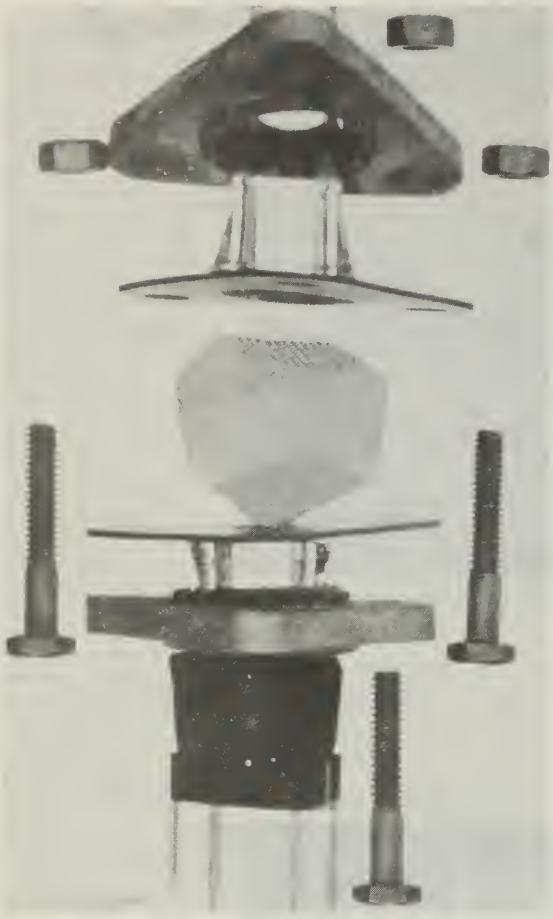


FIGURE V

Column Connection Hardware

cycler batchwise in our experiments, however, the cycler can be installed onto a slip stream in any refinery and accurate field tests conducted on-site with minimum up-keep.

In order to operate the cycler for extended periods of time without attention, a rugged, reliable column assembly is required. This consists of a jacketed, heavy walled glass column with flanges at both ends (Sentinel Glass Co., Hatboro, PA). The resin is retained at both ends by a "dutch weave" metal screen which is held by a flange set. This consists of a metal flange on each column end with a fiber insert to avoid a metal to glass contact. The two flanges-one on each of the two glass pipes to be connected-are held together through nuts and bolts. Between the two glass pipes is a rubber gasket, screen and another gasket. The result is a very secure joint holding the retaining screen. The resin can be removed easily from this system by loosening the nuts at one end. Details of the connection fittings are shown in Figure V. Normally, one-half inch inner diameter columns are used and the resin height is one foot to 15 inches. Extra space-approximately one foot-is left empty for backwashing purposes. This column dimension has been demonstrated to give results within 10% of those of plant size equipment.

ION EXCHANGE DECOLORIZATION PARAMETERS

Cane syrup decolorization is frequently practiced using a strongly basic anion exchange resin operated in the chloride form, with regeneration using aqueous solutions of sodium chloride. The cycling apparatus described here provides a reliable technique for assessing the effect upon decolorization of a number of variables all of which are important in the design of an effective, efficient decolorization system. The pertinent variables are enumerated in the following along with the normal ranges in value:

VARIABLES

Variables	Range
Flow Rate	1-5 BV/Hr.
Throughput	20-200 BV/Cycle
Regeneration Level	13-20 lb. $NaCl/Ft^3$
Regeneration Direction	Concurrent or Countercurrent
Sugar Color (Influent)	100-2000 mau (420 mμ)
Sugar Ash (Influent)	500-2000 ppm (as $CaCO_3$)
Sugar Concentration	60-70° Brix
Sugar Temperature	70-80°C
Sugar pH	7-8

Future studies within our laboratories will center upon producing quantitative effects of each of these variables and their interactions upon decolorization.

RESIN SYSTEMS

Generalized results may be given at this time for resin types in their treatment of syrups. Styrene based resins normally give higher decolorizations early in their life than acrylate based resins. However, this high decolorization falls in extended use or under heavy color loads mainly because the adsorbed color is not completely removed on each regeneration. Acrylate resins do approach perfect regeneration and are known to maintain their decolorization level for years. Usually, the selection of the resin is a compromise between the extent of decolorization required and the desired resin life. Use of these resin types in series give the highest decolorization levels and long life when the acrylate resin is in the primary unit and the styrene resin the polisher. These general conclusions are shown in Figures VI and VII in which laboratory data are shown under a fixed set of conditions typical of many refineries. In Figure VII regeneration efficiency is noted at periodic points along the appropriate curves.

FIGURE VI

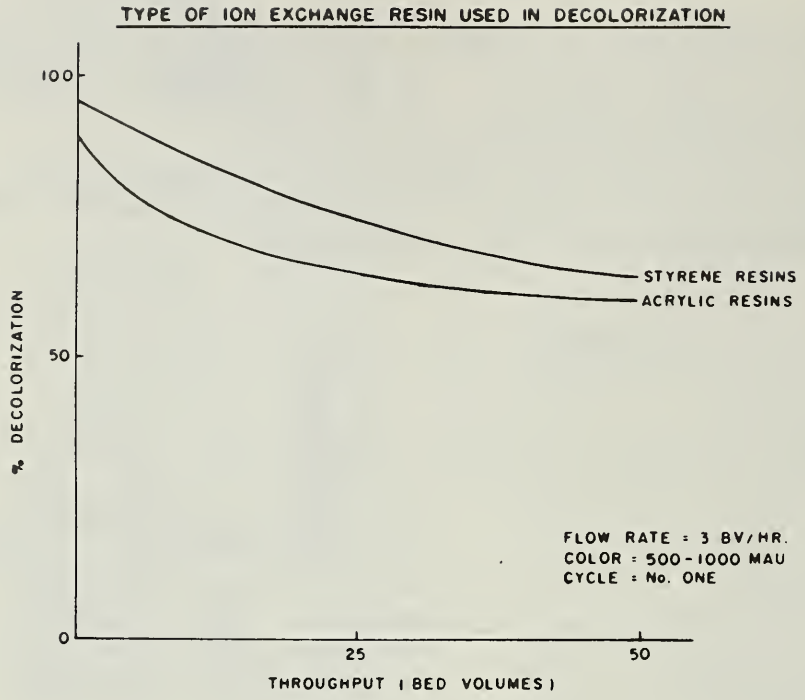
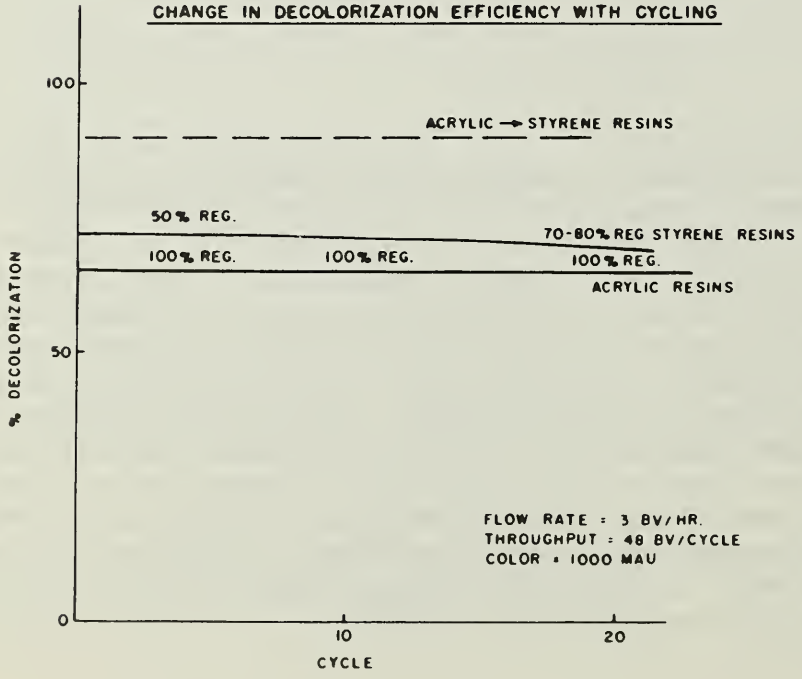


FIGURE VII



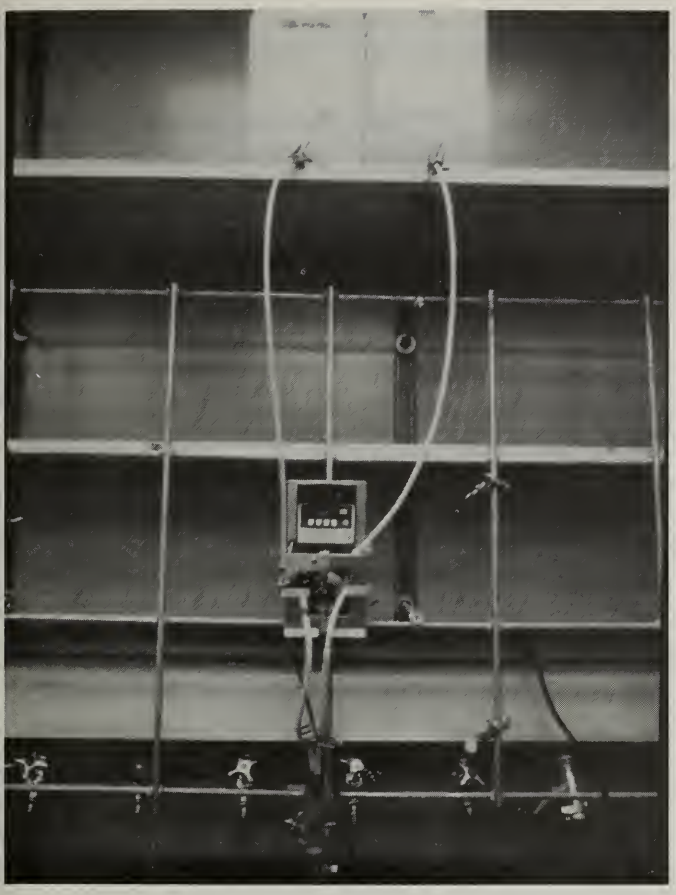


FIGURE VIII

Automatic Microcycler

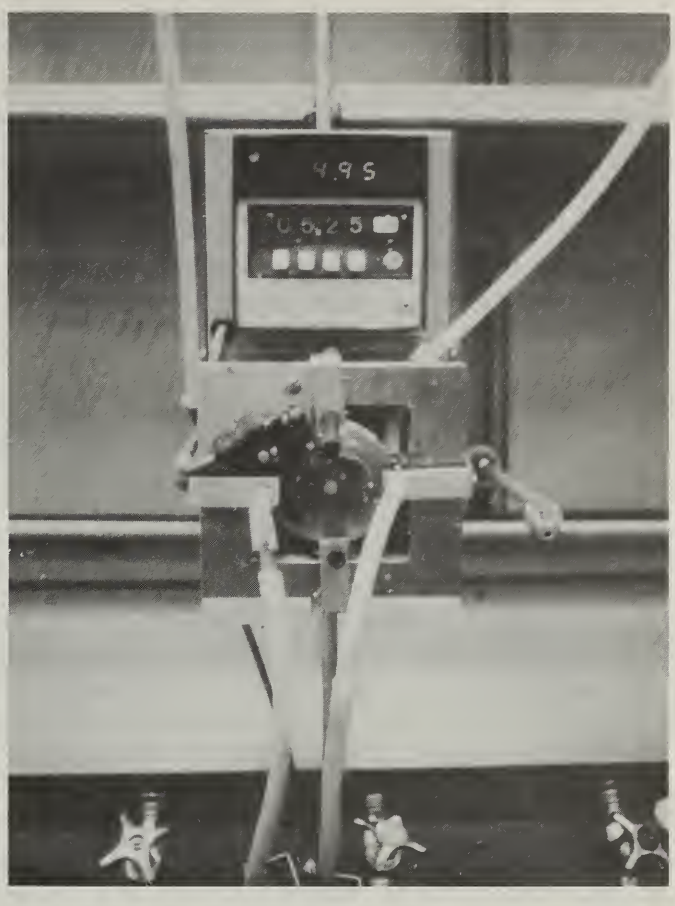


FIGURE IX

Automatic Microcycler

AUTOMATIC, ACCELERATED CYCLING APPARATUS

An apparatus has been developed which quickly cycles an ion exchange resin through any cycle. This is more appropriate for studying factors which can be accelerated without causing major changes in results. Resin stability is one such factor. Cycling between sugar solution and water can simulate shrinking and swelling in 15 minutes and give the equivalent of full resin life in a month or less. On the other hand, sugar decolorization and the subtle organic fouling that may occur cannot be accelerated by this apparatus.

This apparatus consists of a very slow speed motor which can be set from approximately 10 cycles/minute to 1 cycle/4 hours. The motor is controlled electronically by a digital-control and readout-timer. Solution feed lines pass from the reservoirs through a specially designed head which physically pinches off the tubing. The pinching device is a metal cam which is directly attached to the slow speed motor. The cam revolves with the motor drive. A notch, which is removed from this cam, passes over each line of tubing successively allowing flow to a sintered glass tube-a water jacket provides temperature control-which contains the resin. The resin as a result is cycled. Figures VIII and IX.

CONCLUSION

Laboratory techniques and hardware have been devised in which reliable field type data can be produced in the laboratory if the sugar is available or in the refinery itself at 1/10 the manpower usually required. Using this system, ion exchange resins can be studied in terms of their most economic usage as well as synthetically to develop even more effective performance.

DISCUSSION

R. K. Sinha (Calgon): Could you give me some indication of deionizing and inversion control with acrylic base resins?

R. W. Walker: The acrylic resins work very well indeed in deionization. Normally the critical factor where a strong base resin is used is removal of silica or weak acids. The silica leakage for these resins operating in the hydroxide form is very low and every bit as good as for the styrene resins.

There is a limitation which applies when the resin is operated in the hydroxide form for deionization as contrasted to chloride form and that is that it is necessary for the regeneration temperature when you regenerate with caustic be no higher than 35°C (95°F). At that temperature there is excellent removal of the silica and the resin has good life.

F. G. Carpenter (CSRRP): It seems to me that there are 2 types of shocks that break up the resin. One is the osmotic shock in going from 60 Brix sugar to water. And then there is the volume change which you get when you change the form. This can be quite large. Do you have a system that will cycle this form of shock?

R. W. Walker: Yes we do. This volume change is particularly great when going from hydroxide form to chloride or sulfate form. We do a lot of work with acid-base cycling and determine stabilities in that fashion.

And then we have torture chambers where along with this cycling, we pump the resin with great force against metal surfaces. This is perhaps the most extreme condition we run into.

F. G. Carpenter: Nobody in his right mind would pump the resin with great force against a barrier, but in the normal use the resin does cycle through various forms and from sugar to water solution. Do you have a standard life test that you recommend for evaluating resin life in the sugar application?

R. W. Walker: We have not one but a battery of tests, and we are seeking a correlation with field results. We will probably have to use at least 3 or 4 stability tests. The test in which the resin is pumped against the metal plate is realistic. Some people actually do things like that. The test was developed in Japan and correlates well with resin life in a continuous ion exchange process.

J. F. Dowling (Refined Syrups): Which is the greatest shock: Sucrose to water, temperature shock, or chloride to caustic.

W. Fries (Rohm and Haas): That depends upon the resin. Usually the change in ionic form is more strenuous. Most resins can take the osmotic shock very well. We design our resins not to break down, but the most stress is in the change in ionic form.

J. F. Dowling: Is the loading with color bodies and then regeneration with brine a serious shock?

W. Fries: We see no real swelling just by the loading itself. We are concerned about the poisoning effects of the colorants but not the shrinking and swelling shock.

J. F. Dowling: Have you checked osmotic shock at 65 and 70 brix? Is this significantly more of a shock than at 60 brix?

W. Fries: We have worked only to 60 brix and up to this level the osmotic shock is not great.

R. W. Walker: I detect that there may be interest in higher concentrations than 60 brix.

F. G. Carpenter (CSRRP): Many sugar refineries operate at 66 to 68 brix.

R. L. Knecht (Colonial, Gramercy): You mentioned, very briefly, a divinyl benzene-styrene crosslinked resin with no functional groups. What kind of color removal were you getting with this particular resin and have you tried that in series with IRA-900?

R. W. Walker: This is XAD-2 which we call a synthetic adsorbent. There is a paper later in the session on using it for analytical purposes. It does not give as good color removal as strong base resins in the chloride form. It is a more hydrophobic adsorbent, and does not work as well for polishing or gross decolorizing.

R. L. Knecht: Did you try using it in series prior to IRA-900 to prevent irreversible fouling of the strong base anionic resin?

R. W. Walker: No, we did not try any series work.

K. M. Bansal (Calgon): What is the mechanism of decolorization? Is it physical adsorption or ion exchange?

R. W. Walker: It is largely physical adsorption. There is a slight amount of ion exchange.

THE IDENTIFICATION OF VOLATILE CONSTITUENTS IN SUGARCANE AND CANE SUGAR PRODUCTS

Mary An Godshall*, Michael G. Legendre+, and Earl J. Roberts*

ABSTRACT

A novel method of direct elution of volatile compounds for analysis by gas chromatography and mass spectrometry (GC/MS) has been utilized to identify major and minor aroma constituents in cane sugar products. Twenty-three compounds were identified in one sample of blackstrap molasses. Volatiles in fresh cane leaves, frozen cane juice, and raw sugars were also examined. It is possible to use this method to detect differences in raw sugars and to determine if volatiles are formed during processing or derive unchanged from the cane plant.

INTRODUCTION

Knowledge about the volatile constituents responsible for the aroma profile of any food is an important adjunct to the formulation of a successful product. This is especially important when a product undergoes a great deal of processing, as is the case with production of cane sugar and cane sugar products. With the advent of GC/MS techniques, it has become possible to refine and extend the information available on the kinds and amounts of volatile constituents present in foods. However, most methods used for the collection of volatiles require time-consuming distillation and/or extraction procedures. These methods have the disadvantage that the low molecular weight (≤ 100), extremely volatile constituents are, in large part, lost or not present in an amount proportionate to that in the original material. The formation of spurious products due to extraction procedure is also possible with these methods. The recent development of an external sample inlet for direct elution of volatiles onto a GC column (17) has helped to overcome these difficulties.

In the present study, the volatiles in a sample of blackstrap molasses were examined using the direct-sampling technique in conjunction with GC and GC/MS. Many studies have been done on characterization of different molasses fractions (3,6,7,10,12,13,24,28), and a large number of both volatile and non-volatile components have been reported that contribute to the flavor and aroma. Many of these constituents are responsible for the sweet notes in molasses (12). A summary of these findings is listed in Table 1, but it should be noted that this is by no means an exhaustive listing. However, it did not seem likely that the identified constituents were responsible, alone or in combination, for the very characteristic "green" or "grass-like" aroma of molasses.

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TABLE 1 Partial list of constituents previously identified in molasses that contribute to aroma and flavor

Constituent	Ref. No.
Acetaldehyde	10,24,28
Acetic acid	13,28
Acetone	13,28
Acetyl benzaldehyde	10
2-Acetyl furan	28
Acetyl pyrrole	28
Anisole	28
Benzoic acid	7,28
Benzyl formate	28
Butanal	10,24
Butenal	10
n-Butyl benzoate	12
n-Butyric acid	28
m-Cresol	7
Decanal	10
2-Deceno-5-lactone	6
Diacetyl	10
2,6-Dimethoxyphenol	7
Ethanol	28
Ethyl acetate	28
Ethylallomaltol	12
Ethyl benzoate	28
Ethyl formate	28
Ethyl n-hexanoate	12
Ethyl phenyl acetate	12
Formaldehyde	10,24
Formic acid	13
Fural	10
2-Furfural	24,28
Furfuryl alcohol	28
Furfuryl ethyl ether	28
Glyoxal	24
Guaiacol	7,13,28
Hexanal	10
p-Hydroxybenzoic acid	7
o-Hydroxybenzyl alcohol	7
p-Hydroxybenzyl alcohol	7
Hydroxymethylfural	10,24
Isoamyl alcohol	28
Isobutyl alcohol	28
Isobutyric acid	13
Isomaltol	8
Isopropyl benzoate	8

TABLE 1 Partial list of constituents previously identified in molasses that contribute to aroma and flavor--Continued

Constituent	Ref. No.
Isovaleraldehyde	24
Isovaleric acid	28
Maltol	12
Methional	10
o-Methoxy benzaldehyde	28
Methyl benzoate	28
Methylbutanal	10
2-Methyl-2-butanol	28
5-Methyl-2-furaldehyde	28
Methyl glyoxal	10,24
2-Methyl-5-hydroxy-6-ethyl-pyrone	12
Methyl propanal	10
Methyl propyl furan	28
Octanal	10
Pantolactone	12
Phenetole	7,28
Phenol	7
Phenylacetic acid	7,12
β-Phenyl ethyl acetate	28
Phenyl ethyl alcohol	28
β-Phenylpropionic acid	12
Propanal	10
Propanol	28
Propenal	10
Propionic acid	13,28
Resorcinol	7
Salicylic acid	7
Syringaldehyde	13
m-Toluic acid	12
o-Toluic acid	12
Valeric acid	13,28
δ-Valeroactone	28
Vanillic acid	7,12,24
Vanillin	7,12,13

Many of the constituents identified in molasses (and raw sugar) are the result of carbohydrate degradation by means of a variety of pathways including acid, thermal, and Strecker degradation, and nonenzymic browning, with a large number of possible products. These same pathways also lead to formation of high molecular weight polymeric coloring material. Numerous studies with model systems have helped to elucidate some of these pathways.

Wiggins (25) observed that acid hydrolyzed molasses heated with ammonia gave a variety of pyrazine derivatives. Shibamoto and Bernhard (23) showed the formation of 35 pyrazine derivatives from the reaction of L-rhamnose with ammonia and Hodge, et al., (9) discussed the formation of pyrazines and furans from sugar-amine reactions. Hodge (8), in an excellent review, has attempted to integrate and summarize how the pathways interact to produce volatile compounds and browning compounds.

In addition to identification of molasses volatiles in this study, the volatile constituents in fresh sugarcane leaves were partially identified by GC/MS with the intention of determining whether any volatiles in the cane plant persist throughout the refinery into the various products.

EXPERIMENTAL

The molasses used in this study was a South American blackstrap molasses, 75% solids, obtained from the New York Sugar Trade Laboratory. Two raw sugars, one with a normal, pleasant raw sugar odor and the other with an objectionable yeasty odor were used for comparison of volatile profiles. Cane leaves were obtained from a local field in Louisiana and examined within a few hours of cutting. Cane juice, freshly frozen, came from the U.S. Sugarcane Field Station, Houma, Louisiana.

Source of standards: 2-Methyl-3-oxo-tetrahydrofuran was synthesized according to the method of Gianturco, et al. (5). All other chemicals were purchased from reliable commercial sources.

Gas chromatographic conditions: Comparison of retention times and sensory evaluation were carried out on a Hewlett-Packard Model 5750 Gas Chromatograph equipped with dual flame ionization detectors. The column used was stainless steel, 15 feet long, 0.085 in., i.d., packed with Tenax-GC*, 35/60 mesh, coated with approximately 6% poly-MPE*. Helium was used as the carrier gas at a flow rate of 40 ml/min. The detector temperature was 290°C.

Sensory evaluation of the compounds was accomplished by blowing out the detector flame just as a peak began to emerge on the chromatogram and noting the odor of the compound as it emerged from the detector. The major contributing volatiles were immediately detectable in this manner.

Collection of volatiles: The gas chromatograph was fitted with an external injection port assembly based on the method of Legendre, et al. (17). Figure 1 shows a diagram of the assembly. For standard GC operation, the condenser was omitted. (It is, however, necessary for use with GC/MS.) The inlet was modified for use on the HP-5750 GC to accommodate a larger

*Products of Applied Science Laboratories, Inc.

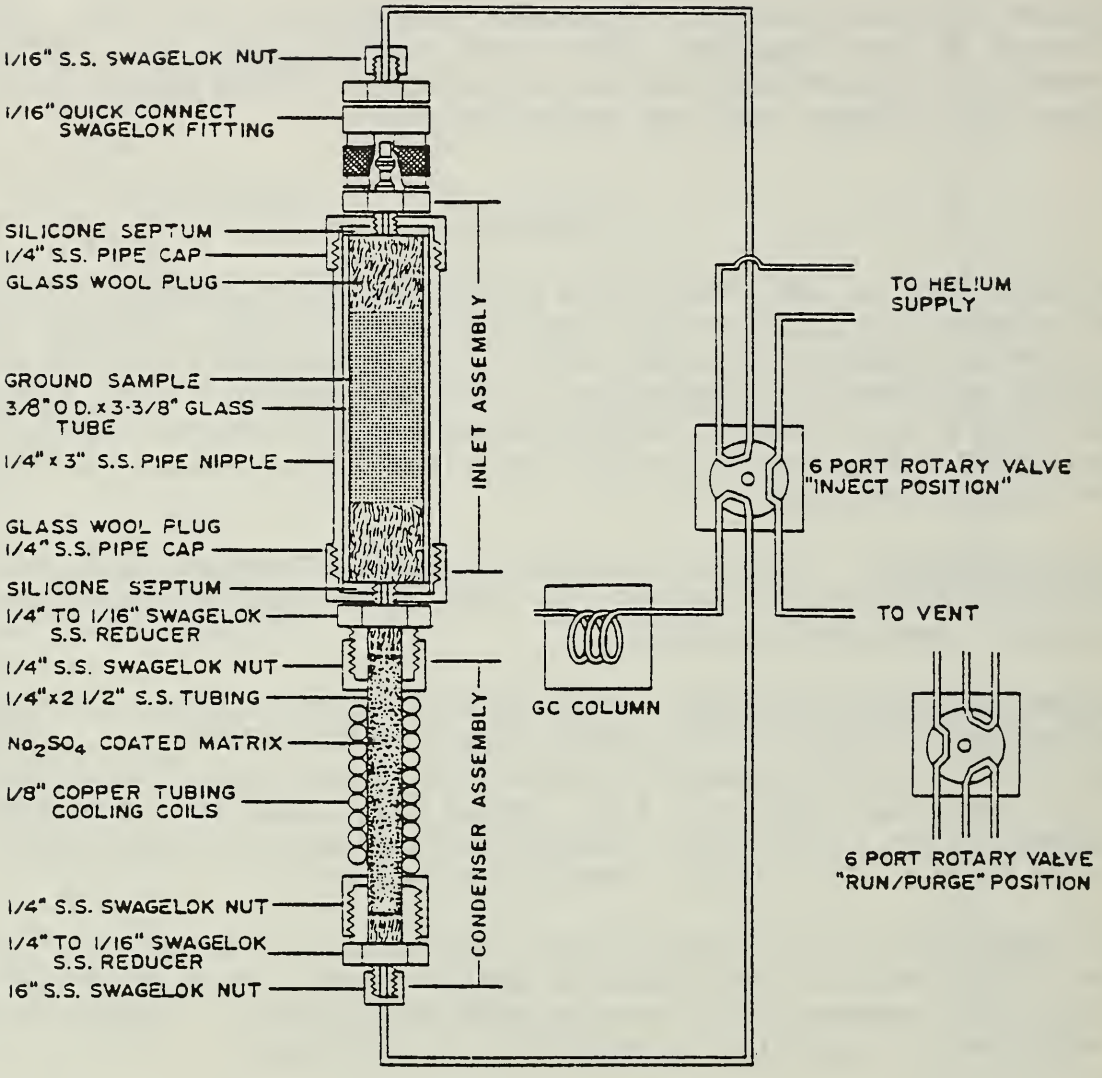

Figure 1. Diagram of inlet used to analyze volatile constituents by GC/MS.

sample by using 4-3/4 in. x 1/2 in. O.D. glass tubing to hold the sample instead of 3-3/8 in. x 3/8 in.; a 3/8 in. x 4 in. stainless steel pipe nipple held the glass tubing in place. This was wrapped with heater tape to achieve uniform heating of the sample during collection of volatiles.

Molasses was sampled by using a spatula to coat 100 to 300 mg of molasses onto a 2-1/2 in. x 5/32 in. glass rod; the coated rod was lightly wrapped with a thin layer of volatile-free glass wool and placed inside the glass liner. The rod was held in place with glass wool plugs. Raw sugar was sampled by placing a plug of glass wool at one end of the glass tube; the tube was filled to within 0.5 in. of the top of the tube with approximately 3 g of very loosely packed raw sugar; the top of the liner was packed with another plug of glass wool to hold the sample in place; 0.05 to 0.1 ml H_2O was injected into the bottom of the sample. The combined effect of helium flow and water vapors rising through the sample facilitated the stripping of volatiles. Cane leaves were sampled by placing 0.3 to 0.7 g finely macerated leaves between two glass wool plugs in the glass sample liner. Cane juice was sampled by injecting 0.1 to 0.2 ml into a glass wool packed liner.

The prepared sample was placed into the external inlet assembly and sealed in place with the septum-lined pipe cap. The six-port rotary valve was set to the "inject" position and the inlet system heated with the heating tape at 135°-145°C for periods of time ranging from 12 min to 30 min. Cane leaf volatiles were initially sampled without being heated so as to prevent formation of heat-produced artifacts. During the elution time, the helium was swept through the sample, depositing the volatiles at the head of the GC column, which was cooled to 25°C by a stream of air. This allowed the volatiles to collect at the head of the column, without separation on the column. After the elution period, the rotary valve was switched to the "run/purge" position and the volatiles were separated with temperature programming from 30°C - 210°C at 4°C/min. The glass liner with sample was removed, replaced with an empty glass tube in order to maintain a seal, and the inlet assembly purged with air to the atmosphere during the GC run.

Authentic compounds, used for determining retention times, were sampled in a similar manner: A small amount of glass wool was placed inside a glass sample tube and 1 - 2 µl of a dilute sample (∿100 - 1000 ppm) of standard was injected into the glass wool. The sample was then subjected to the same elution conditions as the molasses samples.

Since retention time alone is not always a reliable method of identifying compounds, especially in the case of many closely-eluting peaks, a peak enhancement technique was developed that avoided the uncertainties of relying on retention time alone. A sample was prepared in the manner described above and enhanced with a 1 µl injection of a dilute solution of one or more authentic compounds into the glass wool layer surrounding the molasses. The sample was run in the usual manner, and the enhancement of the peak or peaks in question relative to a previous unenhanced molasses constituted satisfactory confirmation of identity when coupled with sensory and mass spectral data. This same method was used with the other materials examined.

Mass spectrometry: Direct GC/MS analyses of molasses and cane leaf volatiles were conducted on a Tracor-222 Gas Chromatograph equipped with dual hydrogen flame detectors. A Tenax-GC column coated with 6-7% poly-MPE, 8 feet long x 1/8 in. O.D. was used. The chromatograph was interfaced with a helium silicone membrane separator to a Hewlett-Packard 5930A Mass Spectrometer. The operating parameters were: 70eV ionizing potential, scan range 21-350 AMU in 2 seconds. An INCOS-2000 Mass Spectrometer Data System was utilized.

Samples of molasses were analyzed in a manner similar to that already described for GC with the exception that volatile components were swept from the sample through a condenser packed with Na_2SO_4 coated glass wool to eliminate sample moisture before entering the mass spectrometer. Inlet temperature was 140°C; elution time was 15 min. Cane leaf volatiles were collected in the inlet at 45°C for 25 min. All other conditions were similar to those of the molasses analysis. After the elution period, the rotary valve was put into the "run/purge" position, the GC/MS interface valve was opened, and the GC oven was heated rapidly to 80°C. Once at 80°C, the ion source and data system were turned on and the GC oven programed to 220°C at 4°C/min. With the GC/MS run in progress, the condenser was heated at 150°C while being purged with helium gas to the atmosphere and cooled in preparation for the next sample.

It should be noted that several samples of one blackstrap molasses and one sample of cane leaf were the only samples examined by combined GC/MS. The other products were examined solely by GC.

RESULTS AND DISCUSSION

Volatile constituents in molasses: Table 2 lists the compounds that were identified in the molasses. Although identified by their mass spectra, with the aid of mass chromatograms, several pairs of compounds, i.e., 2- or 3-methyl furan/diacetyl and 2,5- or 2,6-dimethyl furan/2,3 pentanedione could not be individually confirmed by GC retention data and peak enhancement because they had identical retention times. However, their corresponding peaks were individually enhanced by each compound, and diacetyl and 2,3-pentanedione were additionally identified by their powerful and characteristic odors at the exit port of the detector. Dimethylpyrazine was found and tentatively identified as the 2,5-dimethyl derivative although 2,6-dimethylpyrazine could not be ruled out because of similar fragmentation pattern on MS and identical retention on GC.

Figure 2 shows a typical chromatogram of molasses volatiles. Good reproducibility of molasses and raw sugar volatiles was obtained over a collection period ranging from 12 to 30 minutes with only a slight increase in relative quantity of volatiles collected with increased time. It was, however, important to maintain the inlet temperature within a narrow range, 135°C-145°C. At lower temperatures, the reproducibility from sample to sample was poor, with smaller peaks often not appearing.

Table 2. Volatile constituents identified in molasses.

Peak No.	Constituent	Method of identification		
		M.S.	GC retention & enhancement	Sensory
1	Methanol		+	+
2	Acetaldehyde	+	+	+
3	Unknown			
4	Unknown			
-	Sulfur dioxide*	+	+	+
5	Ethanol	+		
6	Unknown			
7	Furan	+	+	
8	Acetone	+	+	
9	Carbon disulfide	+	+	+
10	Dimethyl sulfide	+	+	+
11	2-Methyl propanal	+	+	+
-	Hexane*	+		
12	2- or 3-methyl furan	+	+	
12	Diacetyl	+	+	+
13	Ethyl acetate	+	+	+
14	2-Methyl butanal	+	+	+
15	2,5-Dimethyl furan	+	+	
15	2,3-Pentanedione	+	+	+
16	Acetoin	+	+	+
17	Unknown			
18	2-Methyl-3-oxo-tetrahydrofuran	+	+	+
19	Furfural	+	+	+
20	Furfuryl alcohol	+	+	+
21	Unknown (43, 86, 73, 116)**	+		
22	2,5- or 2,6-Dimethyl pyrazine	+	+	
23	Substituted furan (81, 53, 126, 80)	+		
24	Furyl methyl ketone (2-acetyl furan)	+	+	+
25	Substituted furan (81, 98, 43, 140)	+		
26	Furyl ethyl ketone	+	+	
27	Unknown (134, 74, 105, 50)	+		

Note: Compounds with the same peak number have the same retention time. Peak numbers correspond to peak numbers in Figure 2.

* Seen on MS only.
** Numbers in parentheses refer to major ions of the mass spectrum.

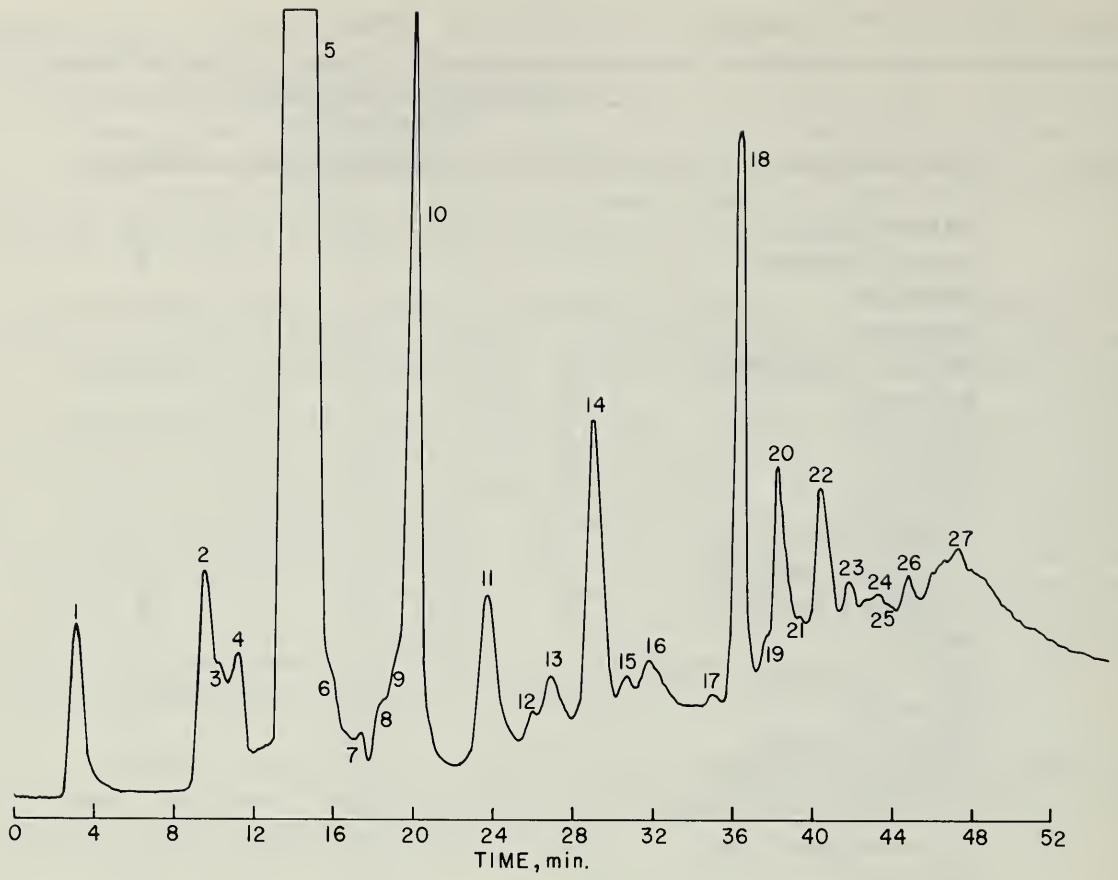

Figure 2. Gas chromatogram of molasses volatiles. Peak numbers are identified in Table 2.

A Vigreaux column low hold-up distillation of a 50% solution of the molasses was done to determine which were the most volatile compounds and thus the ones that contributed most to the molasses aroma. The distillate had the typical molasses aroma. The constituents in the distillate were identified by GC and GC/MS to be: Acetaldehyde, dimethylsulfide, 2-methyl propanal, diacetyl, 2-methyl butanal, 2,3-pentanedione, and 2-methyl-3-oxo-tetrahydrofuran. Methanol and ethanol were also major components of the distillate. However, these alcohols have high flavor thresholds (4,22) and are thought to contribute very little to the overall impression.

During this distillation, it was noted that a powerful molasses aroma was exiting from the vent. A short length of rubber tubing was attached to the vent, and this was bubbled into 1 ml water cooled in an ice bath. After 20 min of collecting, a GC run (Figure 3) showed that the only major component trapped in the ice water was dimethylsulfide, offering the first clue to its importance in the molasses aroma complex.

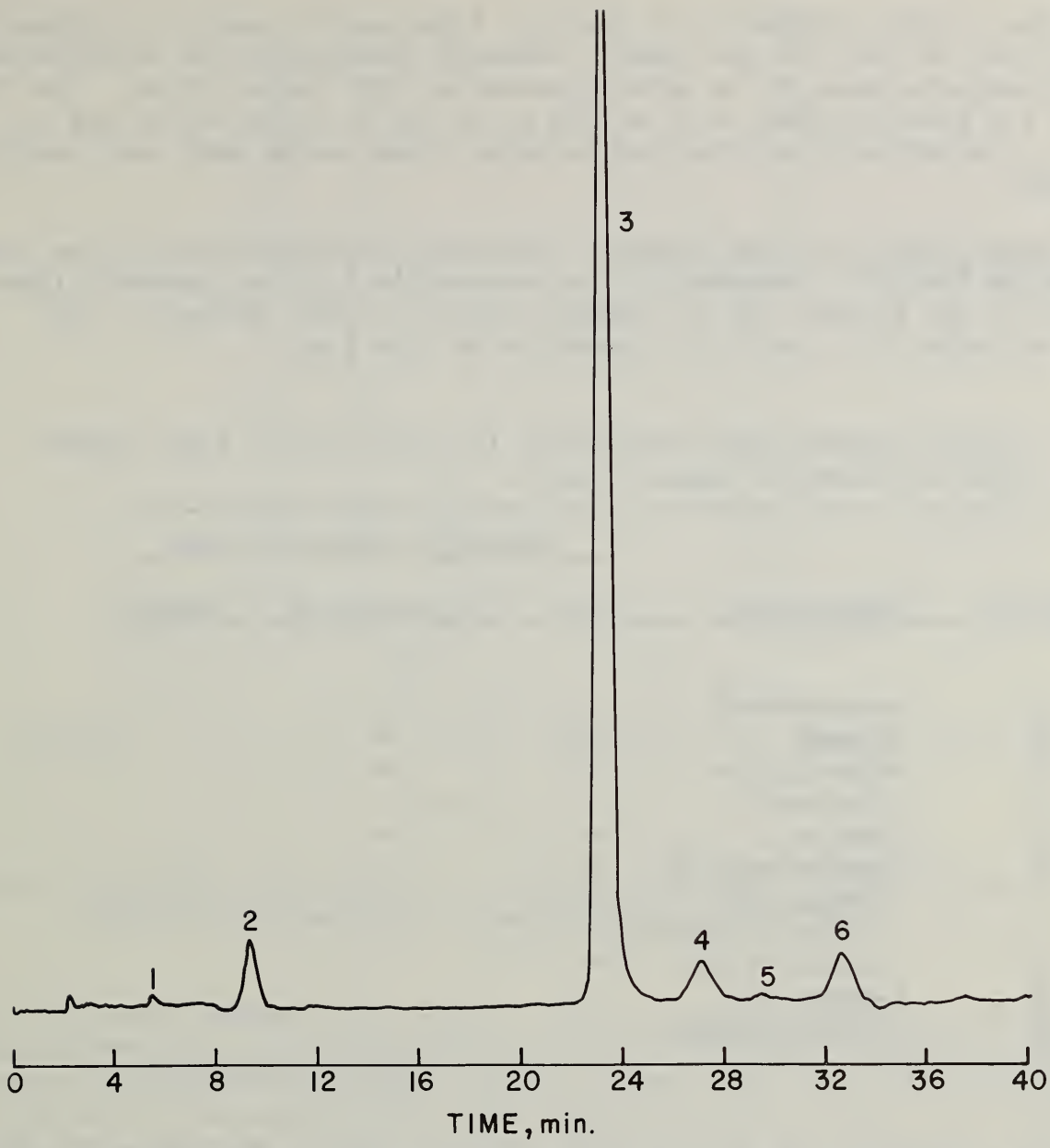

Figure 3. Gas chromatogram of dimethylsulfide in vapors from molasses distillation: Collected in ice water for 20 min. (1 = methanol; 2 = acetaldehyde; 3 = dimethylsulfide; 4 = 2-methyl propanal; 5 = diacetyl; 6 = 2-methyl butanal.)

It is interesting to note that in 1953, Binkley and Wolfrom (2) isolated a volatile extract from cane molasses with strong molasses odor whose infrared spectrum indicated the possibility of a sulfur function. This finding was not pursued further, and as far as can be determined, the present report is the first identification of dimethylsulfide as a component of molasses.

These findings indicate that the characteristic aroma of molasses is influenced by two major factors: (1) The sweet, caramel component contributed by such constituents as diacetyl, 2-methyl propanal, acetoin, and furfural; and (2) the strong "grassy" or "green" component contributed by dimethylsulfide.

Furfural has a flavor threshold in water of 3 ppm and is used as a caramellic food flavoring in the 1-30 ppm range. Although dimethylsulfide is malodorous in large concentrations, it is quite pleasant at low concentration. Its flavor threshold has been reported to be as low as 12 ppb in water and 19 ppb in milk (1). A solution of several ppm in water alone has an odor very reminiscent of molasses.

Volatile constituents in cane leaves: The compounds identified in cane leaves are listed in Table 3. 3-hexen-1-ol is responsible for the intensely fresh green odor of all grasses and is commonly known as "leaf alcohol." The identity of peaks 8, 9, and 10 is tentative at this time.

Table 3. Volatile constituents identified in cane leaves. Peak numbers refer to those in Figure 4 and 5.

		Method of Identification		
Peak No.	Constituent	M.S.	GC retention	Sensory
1	Acetaldehyde		+	+
2	Ethanol	+	+	
3	Acetonitrile	+	+	
4	2-Propanol	+	+	
5	Acetone	+	+	
6	Dimethylsulfide	+	+	+
7	3-Hexen-1-ol ("leaf alcohol")	+	+	+
8	2,4-Hexadienal	+		
9	1-Hexen-3-ol	+		
10	2,4-Heptadienal	+		

Figure 4 is a chromatogram of cane leaf volatiles from 0.7 g cane leaf eluted at 25°C for 20 min in the inlet. Figure 5 is a chromatogram of the volatiles eluted from 0.5 g cane leaf collected in the inlet for 16.8 min at 70°C. The dimethylsulfide peak had increased relative to its peak in Figure 4. When the same material from Figure 5 was rechromatographed after a volatile collection period in the inlet for 10 min at 130°C, the dimethylsulfide peak had increased about a hundredfold. In another sample, upon heating the leaves, the dimethylsulfide content increased a thousandfold, based on integration counts.

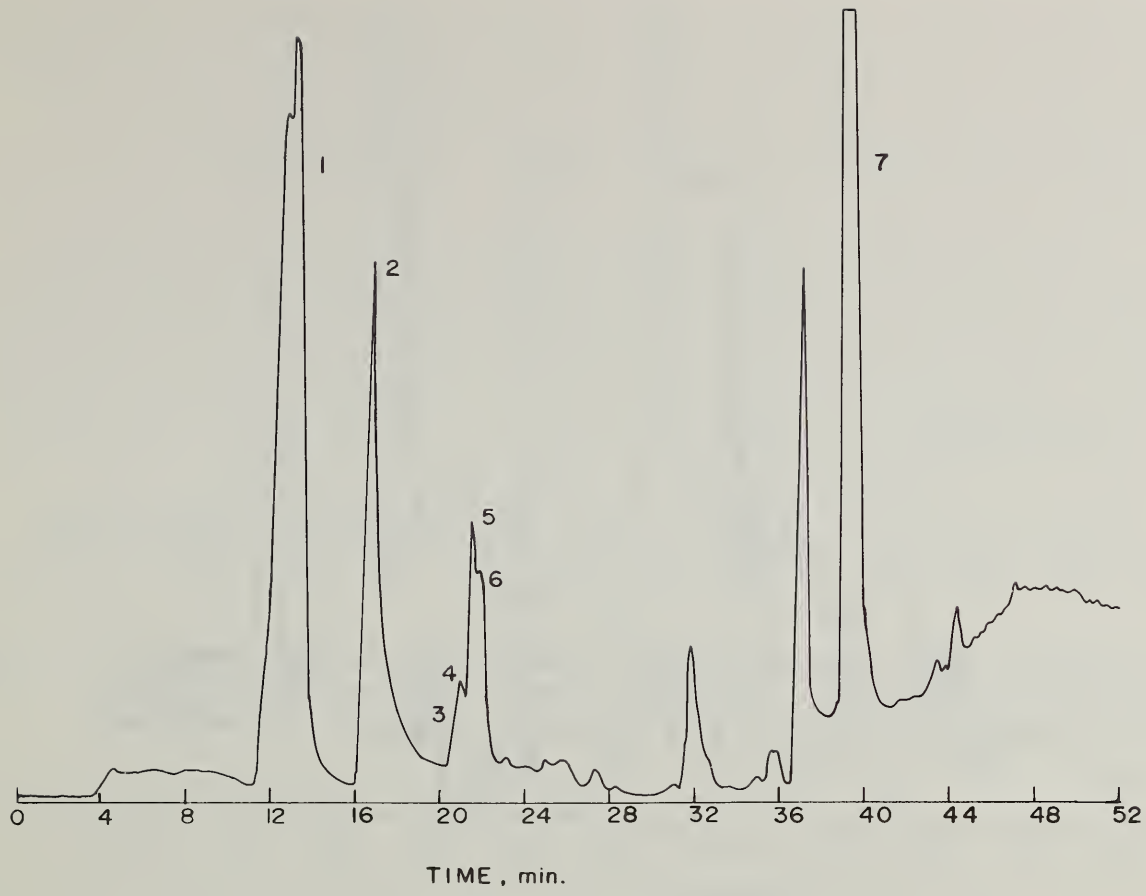

Figure 4. Volatiles eluted from 0.7 g cane leaves at 25°C for 20 min. (Peaks with numbers are identified in Table 3.)

The leaf alcohol (3-hexen-1-ol), peak 7, also increased markedly with heat but was not thought to be a breakdown product of heating. Some of it may be complexed and released on heating. Other changes were obviously occurring since the leaves were essentially being dehydrated and "cooked," as evidenced by their dry appearance and straw color after elution at temperatures above 100°C. The object of the present study, however, was not to monitor the changes that occurred under such extreme conditions except in the case of dimethylsulfide.

The major reason for examining fresh cane leaves was to determine if dimethylsulfide was naturally present in the leaves or formed during processing, since it was so prominent in molasses aroma. Dimethylsulfide is known to be produced during the cooking of many foods (14,18,21), including corn (1), a member of the Gramineae order to which sugarcane belongs. It appears to be present as a minor natural constituent in the cane leaf, but is formed in large quantities via some degradation pathway upon application of heat.

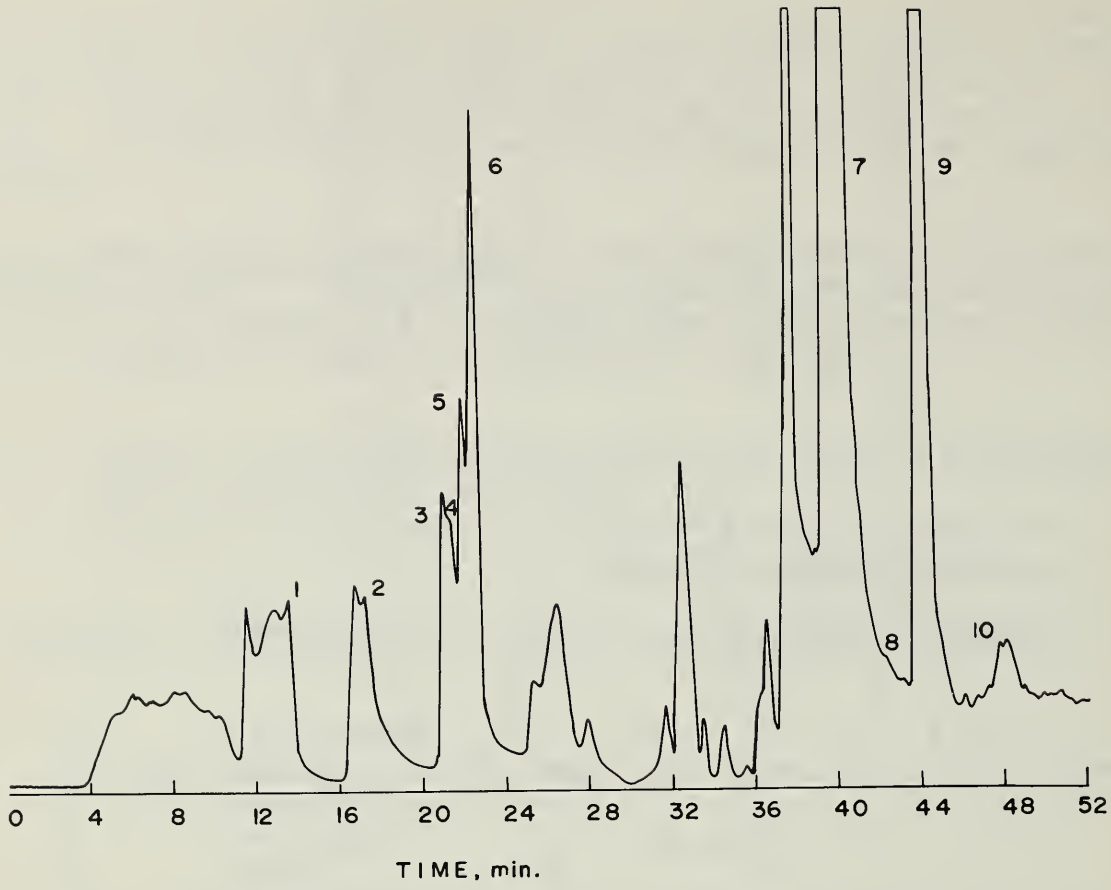

Figure 5. Volatiles eluted from 0.5 g cane leaves at 70°C for 16.8 min. (Peaks with numbers are identified in Table 3.)

There are several pathways by which dimethylsulfide formation can occur: 1.) Strecker degradation of the amino acid methionine (20). However, methionine has not been identified as a free amino acid in cane (16,19,26). 2.) Breakdown of a precursor, S-methylmethionine sulfonium salt, upon heating, into homoserine and dimethylsulfide. This mechanism occurs in corn (1), tomatoes (27), and tea (15), and accounts for some of the flavor changes these foods undergo with cooking. This precursor has not yet been looked for in the cane plant. 3.) Enzymatic formation upon disruption of cells. This occurs with onions and garlic and accounts for their characteristic odors. Substrates for production of these volatiles are derivatives of cysteine, known as alliins (11). Cysteine, however, has also not been identified as a free amino acid in cane (16,19,26).

Since dimethylsulfide is so characteristic of molasses odor and is present in all colored sugar products so far examined, it should be of interest to determine which of these mechanisms is operative, so that the pathway for the familiar molasses odor can be avoided in production of white sugar.

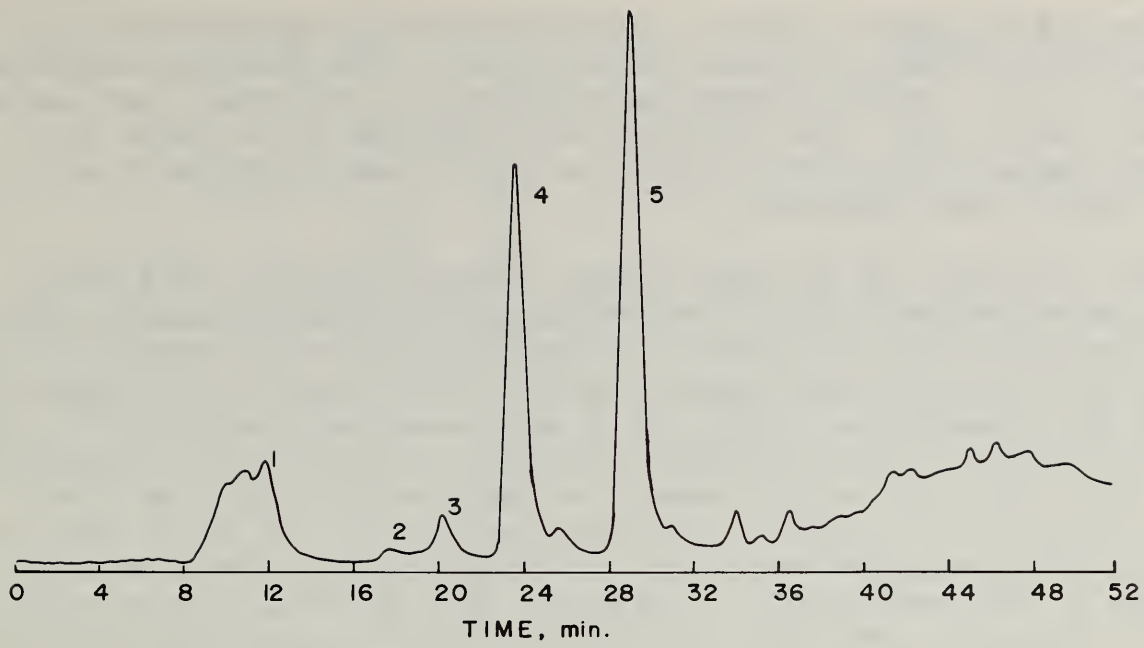

Figure 6. Volatiles in 3.5 g raw sugar with a pleasant odor, eluted at 140°C for 20 min. (1 = acetaldehyde; 2 = ethanol; 3 = dimethyl-sulfide; 4 = 2-methyl propanal; 5 = 2-methyl butanal.)

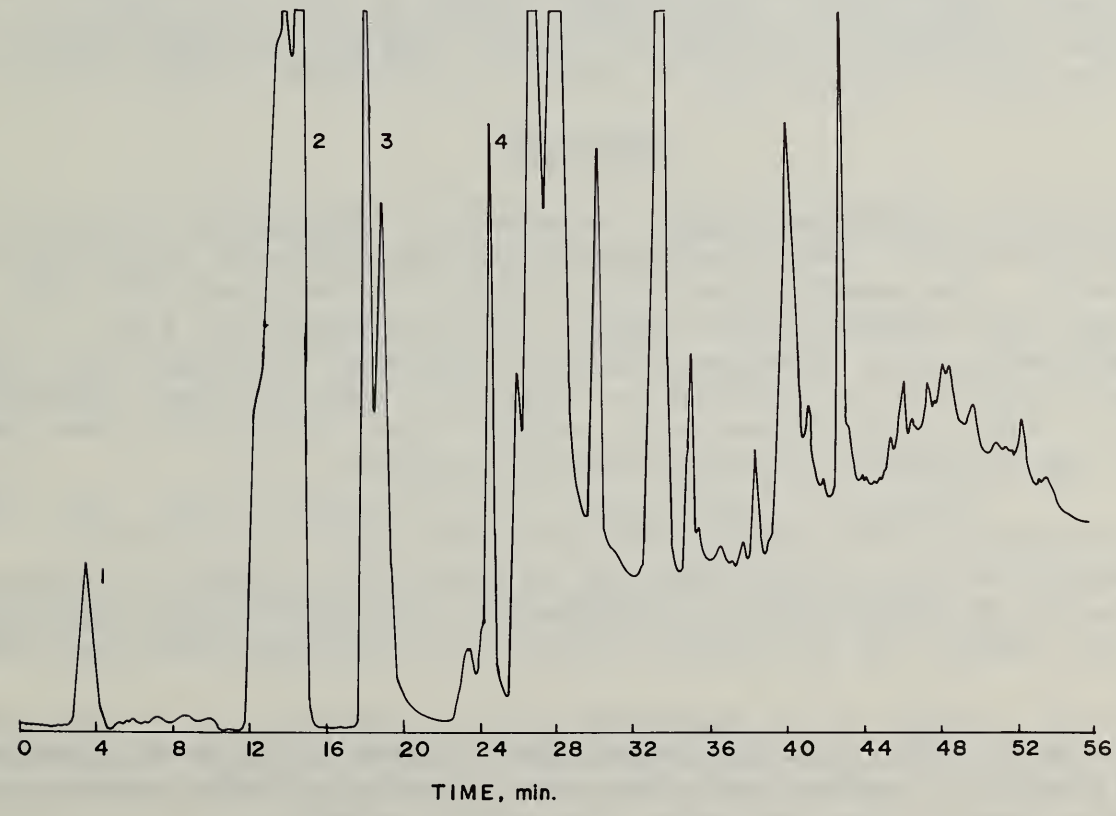

Figure 7. Volatiles in 3.75 g raw sugar with objectionable odor, eluted at 140°C for 16 min. (1 = methanol; 2 = acetaldehyde; 3 = ethanol; 4 = dimethylsulfide.)

Volatiles in raw sugars: Figure 6 shows the volatiles profile of 3.5 g raw sugar with a normal, pleasant raw sugar odor. The volatiles were eluted at 140°C for 20 min. Figure 7 shows the volatiles in a raw sugar that had an unpleasant yeasty odor. The volatiles were collected in the inlet from 3.75 g of sample at 140°C for 16 min. As can be seen in Figures 6 and 7, the differences were dramatic.

The "good" raw sugar has two major peaks, 2-methyl propanal and 2-methyl butanal; there are small amounts of acetaldehyde and dimethylsulfide and a trace of ethanol along with traces of other higher molecular weight volatiles (eluting after 36 min, with molecular weights $\tilde{>}$100) that were not identified. Although the chromatogram in Figure 6 is at a sensitivity setting of 0.4 x the one in Figure 7, the differences in profile are still major, especially in the higher molecular weight range. In order to make sure that these compounds were not artifacts of the inlet temperature, the "good" sugar was treated at the same temperature for an additional 4 min. The consistent appearance of the same profile of volatiles, with no change in the peaks of these compounds, confirmed that the procedure was not producing artifacts.

Volatiles in cane juice: The volatiles in a sample of 0.1 ml freshly frozen Louisiana cane juice eluted at 135°C for 16 min are shown in Figure 8. It is of interest to compare this profile to that of the fresh leaves in Figures 4 and 5. All the 3-hexen-1-ol that appeared as peak 7 in Figures 4 and 5 has disappeared, removed either by volatility loss or enzymatic degradation, since heat does not destroy it. This alcohol is not found in any other sugar product except fresh leaves. The ethanol content in this juice is high, although the cane had not deteriorated prior to crushing and the juice was immediately frozen. Varietal differences may be responsible for some of these observations.

CONCLUSION

This new method of examining volatile compounds in plants and foods has shown great versatility and is certainly promising for use in all areas of the sugar industry. The possibilities for use would include identifying off-flavors formed by problems in processing, packaging materials, shelf life deterioration, etc. The possibilities for standardization of soft sugar and refinery syrup flavors are obvious. The inlet could be used to determine the effect of heat on the formation of desirable and undesirable aroma constituents, and processing could be altered accordingly.

It is to be expected that molasses from different sources will contain some different volatile constituents due to the variety of conditions of production. It is only logical to assume that end products that utilize molasses, such as soft sugars, may be subject to these variations, although in lesser quantity.

In addition to yielding valuable information on reaction pathways of sugar breakdown products, this new technique shows a way to maintain consistency in flavor and odor in the production of specialty sugars.

Methodologies are at present being worked out for the quantitative measurement of the volatiles of interest. Soft sugars are also under investigation.

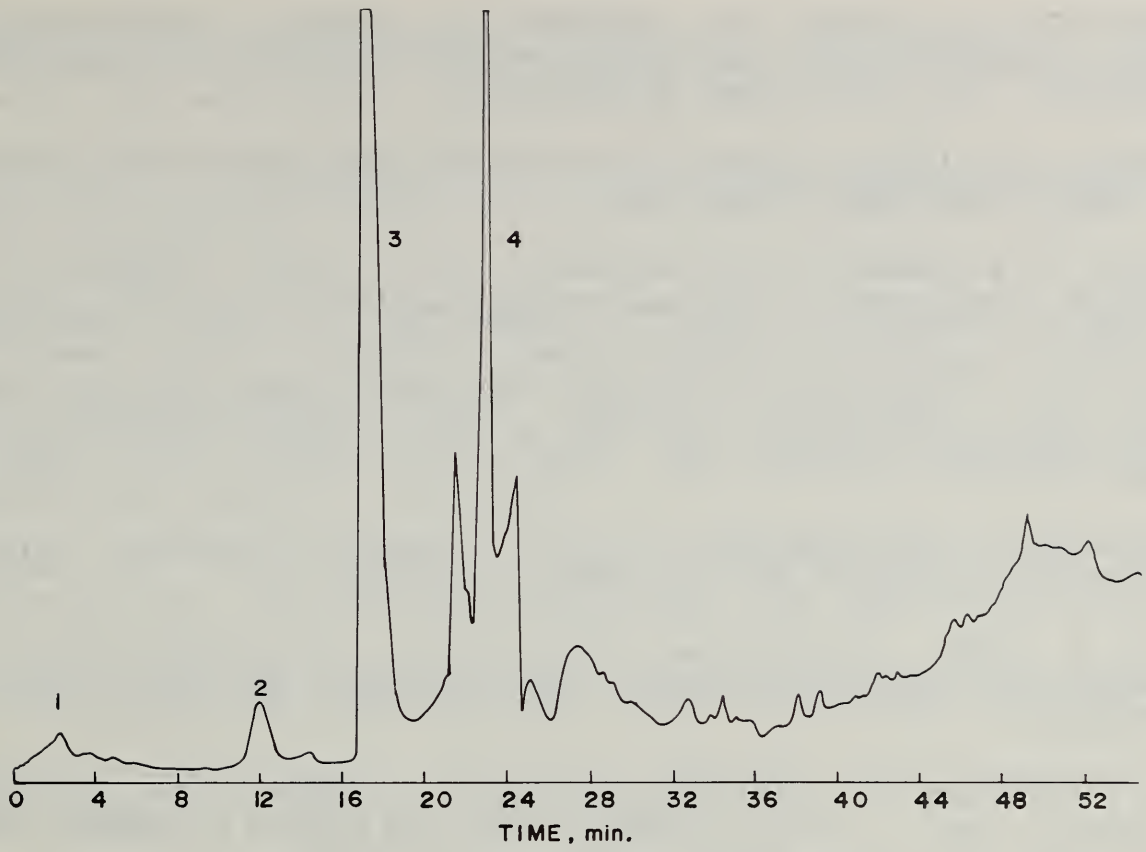

Figure 8. Volatiles in 0.1 ml fresh frozen cane juice eluted at 135°C for 16 min. (1 = methanol; 2 = acetaldehyde; 3 = ethanol; 4 = dimethylsulfide.)

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R. L. Knecht: (Colonial, Gramercy) You very briefly mentioned that you included soft sugars in these evaluations and I think that is the one product that refiners produce where we are selling flavor. Have you done any work on soft sugars and their profiles and do you have any observations as to how these flavors, volatiles, and odors can be more closely controlled in the processing of soft sugars from raw sugar?

M. A. Godshall: We have only started looking at soft sugars and have not completely worked out the method for them. I want to work with them at lower inlet temperatures to make sure that we are getting a true profile of the existing volatiles and not producing anything by the heat. Although I feel the conditions we use for obtaining volatiles--140°C for 16 min--are not very stringent, I want to be very sure that we are not causing reactions to occur in the inlet. We do have several soft sugars on hand that we obtained at the grocery store and we do note differences in volatile profiles looking at them under the same conditions. Once we know more about what constitutes a good aroma we can talk about how to enhance and standardize the flavor.

J. F. Dowling (Refined Syrups): I would like to congratulate the group on doing some fine follow-up work on something we have needed. About 10 years ago we examined the head space gas from molasses by GLC and got a dozen or so peaks.

We found one peak would increase as we heated the sample. We found this with char liquor, medium invert syrup, and granulated sugar. What we sell is a flavor, and these flavors, good or bad, are in the sugar and carry through to the finished food product. I would like to see the Project follow through with this work and determine what is coming through char liquor, what is being created with the heat, and what is in the finished product, and not just limit research efforts to the brown sugar.

Do you plan to collect the individual peaks and identify them? To do this you would have to split the column output, because the flame destroys the sample.

M. A. Godshall: We are already doing that. The gas chromatograph is directly interfaced with the mass spectrometer.

J. F. Dowling: But you have not collected any of the pure compounds off the column. Have you tried to get a pure sample of dimethylsulfide to identify for molecular weight on a moass spec or IR, etc., to verify that it is dimethylsulfide?

M. A. Godshall: We have no doubt that it is dimethylsulfide. We can blow out the flame and smell it at the detector. If you use a large sample of molasses, the DMS almost knocks you out because it smells bad, even though at a low concentration it has a pleasant molasses odor. On the mass spec this peak had a correlation of about 800/1000 with dimethylsulfide, which is excellent for M.S. computer correlations since they are based on data from many different machines and conditions. On the GC the retention time of this peak is the same

as dimethylsulfide and adding dimethylsulfide to the sample enhances the peak. The main thing was identification by the mass spectrum and the odor. The odor was absolutely unmistakable.

F. G. Carpenter: We have 3 gas chromatographs. One is hooked to a flame detector, and much of this work was done on that machine. We have another which is hooked to both a flame detector and a mass spec. In the third, the only detector is a mass spec. Both mass spec's are computerized and have a whole library of compounds, and as each spectrum is obtained it is compared with the whole library which is very large. So you get not only the peak, and how much, but also the best guess of what it is and how well the spectrum matches that best guess. Anything over a 0.5 correlation is considered a good possibility and we were getting a 0.8 correlation with dimethylsulfide.

N. I. James (USDA): Do you have any plans for collecting leaf or juice samples from different varieties of sugarcane?

M. A. Godshall: Not at the moment. Our immediate plans are to continue to identify important volatile constituents in the product sugars and to quantify them rather than to look at the plant sources. This may develop later.

N. I. James: Do you see this as a technique that those of us involved in developing new varieties should take a look at?

M. A. Godshall: I think it may hold great promise for varietal work, but further development of the technique is needed before I could say what direction this type of work would take.

R. Cormier (Redpath): Would you remind me of the temperature at which you run your tests?

M. A. Godshall: The volatiles are stripped from the sample in the inlet at 140°C which translates into 285°F.

R. Cormier: This seems to me a rather high temperature considering that, most of the time, a sugar product is tasted at room temperature. Hence a temperature around 25°C or 37°C, which is the normal body temperature would appear to me to be a better point of comparison, because, after all, when one gets an aroma profile using a gas chromatograph, he substitutes that instrument for a nose.

M. A. Godshall: That is certainly a valid point and one that needs to be taken into consideration when sensory evaluation of products is begun. We use the higher temperature to speed up the stripping of the volatiles from the sample. You can strip at a lower temperature but then more time is required.

R. Cormier: Principles of physical chemistry teach us that the composition of the vapor phase should vary with the temperature applied. Hence some volatiles components with low partial vapor pressure around 30°C will see their volatility increased at 140°C. The profile thus obtained would be distorted in comparison with that which would be presented to a nose at 30°C.

M. A. Godshall: At equilibrium, the composition of the vapor phase varies with temperature. Equilibrium does not exist in the inlet because helium is continuously stripping the volatiles. At a given temperature, whatever is volatile up to that temperature will be volatilized and swept out of the sample.

The resulting chromatogram will give a good indication of relative concentrations of volatiles, if not also their absolute concentration.

R. Cormier: I agree with the fact that you should be recovering almost all the volatiles present in the sample. But, doing so, it is not in my opinion, the best way to get a representative aroma profile because the proportion of the volatiles, one to the other, within the vapor phase is not by any means a function only of their respective concentration but rather mainly a function of their vapor pressure at a given temperature.

Nevertheless this way of doing things appears to me very useful in identifying the low molecular weight components present in the liquid phase.

Are you pleased with the degree of reproducibility you have attained so far in getting your chromatograms?

M. A. Godshall: I would say not yet because we are still working out the method. A lower inlet temperature may be preferable. However, when we use the same conditions, our results are reproducible. We can collect the volatiles at a given temperature over a range of time and attain reproducibility. When the temperature is lowered but the time is not increased, we find not so much a different profile but smaller peaks, indicating insufficient stripping of volatiles from the samples.

R. Cormier: To be more detailed about the reproducibility, would you feel that the ratio of the area under a peak over the others or the area under a peak for a given sample is reproducible enough?

M. A. Godshall: We have not yet decided on a suitable method for quantifying the profiles. Our work at present is mainly directed toward the identification of significant aroma components. The next step, obviously, is to determine the reproducibility of the profile and then to measure the amount of various constituents, with respect to the effect of a change in concentration on the aroma observed.

You mentioned two ways of determining reproducibility, both of which have their merits. We will probably develop a method based on peak area ratios for selected important aroma compounds rather than depend on absolute areas for a given sample. As you know with GC work, any fluctuation of conditions during a run can change absolute area, but ratios usually remain the same within a given set of circumstances. This is why an internal standard is so useful.

R. Cormier: Do you plan to switch to capillary columns?

M. A. Godshall: No, we do not.

J. F. Dowling: Is the column inlet temperature high, like 175°C to 200°C and

the sample cartridge at room temperature or only slightly above?

M. A. Godshall: No, it is the other way around. The column is cooled to room temperature and the sample cartridge, which we call the external inlet, is heated at 140°C to drive off the volatiles. The volatiles collect at the head of the column. After the volatiles are collected, the 6-port valve is switched, and the carrier gas goes directly to the column and the temperature-programmed chromatographic run is begun.

J. F. Dowling: So what you are doing is heating the sample and collecting the volatiles on a cold column. I think that you are producing many of these volatiles by heating the sample at such a high temperature as 140°C. You should sweep the sample without any heat into a cold column.

M. A. Godshall: We heat the sample to get the volatiles out more quickly. We will have to ensure that we are not forming compounds. So far we have no evidence that we are forming compounds. This inlet system has been used at Southern Regional Research Center for two years with many food products and these conditions have been found to be widely applicable. I appreciate that molasses and sugars may be more labile than some other foods, and we will certainly check further, especially for the formation of higher molecular weight compounds.

W. L. Reed (Revere): That was an excellent paper. Some of the volatiles seem to be present all through the sugar refining process and others only appear in the molasses. Is your method quantitative enough to measure these small changes or do you just detect that it is present and may be a new sugar impurity constituent?

M. A. Godshall: We have been concentrating on detection and identification. We already have some idea of approximate concentrations. We are in the process of working out the conditions for getting good quantitative measurements of volatile components and those small changes should be easily measured.

W. L. Reed: How would you account for the increase in dimethylsulfide content with heat in the cane leaves?

M. A. Godshall: This may sound like a contradiction to my previous answers, but dimethylsulfide evidently is formed by heating fresh cane leaves. We feel that it is not present as dimethylsulfide, but that there is a precursor that forms dimethylsulfide upon heating.

A precursor for dimethylsulfide has been found in tomatoes and corn (and corn is a relative of sugarcane) that is called S-methyl methionine sulfonium salt. It is in tomatoes, corn and tea. When heated, it breaks up into dimethylsulfide and homoserine. This reaction apparently occurs as soon as the cane leaves are heated up. The dimethylsulfide is formed at that stage, and goes on into the juice and from there into process. The precusor itself is not volatile.

Although factory molasses contains considerable dimethylsulfide, the raw sugar contains very little. It will be interesting to see whether dimethylsulfide, which is responsible for the molasses odor, is a desirable soft sugar constituent.

SOME OBSERVATIONS ON THE HIGH MOLECULAR WEIGHT COLORANTS IN SUGAR

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CANE SUGAR REFINING RESEARCH PROJECT, INC.*

ABSTRACT

The high molecular weight colorants in raw sugar and the same sugar, washed, were separated by dialysis in bags of molecular weight cutoff values of 3,500, 8,000, and 12,000. The color in the original sugar and that retained in each bag was measured. The color from the washed raw sugar was compared to that of the raw sugar. The total nondialyzable materials from the raw and washed sugars were compared. The nondialyzable material from sugar was subjected to mild hydrolysis and yielded polyphenolic acids. The optical properties of the color in raw sugar and that in the same sugar after being washed were compared.

INTRODUCTION

The color in cane sugar is a complex mixture of plant pigments, melanoidins, and caramels. The plant pigments are principally polyphenols and flavones. Farber, McDonald and Carpenter (1) and Farber and Carpenter (2) identified twenty of these compounds in cane juice. The plant pigments may not themselves be colored but may form colored compounds by reacting with iron or oxygen during processing.

The melanoidins are formed when the reaction products of reducing sugars with amino acids and proteins rearrange to a highly complex mixture of dark-colored polymers. This class of colorants has been studied extensively by Binkley and others (3,4,5); however, no single identifiable component has been isolated.

The caramel colors result from polymerization of decomposition products of sucrose during processing. This class of colorants has been studied by many investigators (6,7) but its composition is still largely unknown.

It is extremely difficult to separate sugar colorants from other large molecules present in a sugar. It appears that some of the color is attached to the indigenous sugarcane polysaccharide (ISP) by hydrogen bonds or covalent bonds, making separation difficult or impossible under mild conditions. If

*This work was done in cooperation with the Southern Regional Research Center, SEA, USDA.

acidic or basic conditions or heat are employed in the separation of colorants, further rearrangements or decomposition are liable to occur so that the isolated color no longer has the same characteristics it originally had.

Because of the complex composition of sugar color, most recent research has focused on its characteristics rather than on structural studies. Tu, Kondo, and Sloane (8) studied the distribution of low and high molecular weight colorants in the manufacturing process. They used Sephadex columns to determine the molecular weight distribution of colorants between that in the outside coating of raw sugar crystals and that occluded within the crystals. They concluded that more high molecular weight colorants are occluded in the crystals than are left in the molasses film on the surface of crystals.

Chou and Rizzuto (9) studied the acidic nature of sugar colorants. They classified the acidic colorants into four groups according to their acid strength. They also found that each group could be selectively desorbed from adsorbents by using bases of different strengths.

Smith (10) separated sugar color into several fractions on Sephadex columns, according to molecular weight, and studied the efficiency of several adsorbents in removing the color in the different fractions. Although a tremendous amount of work has been done on sugar color, little is known about the relative amounts of low and high molecular weight colorants occluded in the crystals and remaining in the molasses.

The objectives of the work described in this paper were, (a) to determine the molecular weight distribution of colorants in raw and washed raw sugar by dialysis in bags of different molecular weight cutoff values; (b) to study the composition of the nondialyzable material in raw and washed raw sugar; and (c) to compare the optical properties of the color in raw and washed raw sugar. It is quite probable that some color molecules are selectively occluded in the crystal. These are the compounds that must be identified, so that their removal in process may be as efficient as possible.

EXPERIMENTAL

Affination of raw sugar: The raw sugar was washed by the Hawaiian method (11). The washed sugar was spread on paper and air-dried at room temperature.

Clarification and color measurement: The sugar was clarified and color measurements were made by ICUMSA method 4 (12) as described below. Sugar was dissolved in an equal weight of water and vacuum filtered through a mat of analytical filter aid on a Whatman number 2 filter paper. After filtration, the pH of each solution was adjusted to 7.0. For color measurements, an aliquot of each solution that contained 25 g of solids (refractometer) was diluted to a volume such that the transmittance was 50% to 80% at 420 nm. The volume was recorded and the color was read on a Talameter.

Dialysis of sugars: For dialysis a quantity of solids of each clarified solution containing 25 g was placed in regenerated cellulose bags with molecular weight cutoff values of 3,500 or 8,000 or 12,000. Compounds of molecular weights below these cutoff points were washed out of the bag. The samples were

diluted in the bags (about 1000 ml capacity) to about 400 ml with deionized water and dialyzed 100 hr against flowing deionized water saturated with toluene. When the dialysis was complete, the solution in each bag was concentrated by ice sublimation. The pH was adjusted to 7.0, and the volume was adjusted to that used in the color measurement of the original solution before dialysis. The color in the solution from each bag was measured with the Talameter. In this way the color remaining in each bag could be directly compared to that in the original solution.

After the color had been determined each solution was concentrated and freeze-dried in a tared vial, and the remaining solids were weighed.

Mild hydrolysis of dialyzate: Two grams of solids from the 12,000 molecular weight cutoff bag was dissolved in 50 ml of 1 N sulfuric acid and boiled under reflux for 1 hr. The solution was cooled and extracted with four 25 ml portions of ether. The ether solution was dried over sodium sulfate. The sodium sulfate was filtered off and the solution was evaporated to dryness. The eresidue was dissolved in 2 ml of ethanol. High voltage paper electrophoresis of the ether extract in 0.05 M sodium tetraborate solution showed 18 fluorescent spots when viewed under ultraviolet light. Thin layer chromatography of the extract on plates coated with silica gel developed with the solvent system, benzene: acetic acid: dioxane (22:1:6), showed a similar number of fluorescent spots when viewed under ultraviolet light.

Absorption spectra of raw sugar before and after washing: Solutions of raw sugar and the same sugar after being washed and clarified as described above were prepared. The solids content was adjusted so that the percent transmission would be 20-80%. The pH was adjusted to 6.0 and an absorption curve

Table I

Color in original sugar sample and that retained in dialysis bags of 3,500, 8,000, and 12,000 molecular cutoff values.

	Sugar No.	Vol. of solution ml	Color in original sample	Color retained in dialysis bags molecular weight cutoff 3,500	8,000	12,000
1.	raw	500	5.00	2.76	2.40	2.20
	washed	100	0.90	0.69	0.52	0.44
2.	raw	250	3.04	1.80	1.63	1.52
	washed	100	0.56	0.54	0.52	0.44
3.	raw	250	3.50	1.55	1.45	1.30
	washed	200	1.20	0.56	0.58	0.52
4.	raw	500	7.40	4.10	3.80	3.40
	washed	200	1.52	0.88	0.72	0.56

was run between 300 and 800 nm on a Beckman DB spectrophotometer using deionized water as the reference. The pH was then adjusted to 7.0 and then to 8.0, and an absorption curve was run at each pH.

RESULTS AND DISCUSSION

Dialysis and concentration by ice sublimation provided a means of separating the color from sugar and other low molecular weight substances without subjecting it to acidic or basic conditions or to heat. In this way the color should not be altered from its original structure. The color was separated into three fractions on a molecular weight basis. Although the color was not separated from other large molecules such as protein and polysaccharides, since these are probably colorless, they should not interfere in the measurement of the color.

The measurement of color in the original sugar and that retained in the three dialysis bags is shown on Table I. The results are shown graphically in Figures 1A, 1B, 1C, and 1D. In all four sugars studied, the percentage of color retained in the 3,500 M.W. cutoff bag was a greater percentage of the total color in the washed sugar than in the raw sugar. In like manner, the color retained in the 8,000 M.W. cutoff bag was a greater percentage of the total color in the washed sugar than in the raw. The color retained in the 12,000 M.W. cutoff bag ranged from 37% to 49% for the raw sugar and 37% to 78% for the washed sugar. This indicates that a greater percentage of high molecular weight colorant is occluded within the crystals than remains in the molasses film on the crystal surface. Compounds below 3,500 M.W. comprise a greater percent of this coating color than of the crystal color. It should be noted that the turbidity in sugar solutions is composed of high molecular weight colloidal material and should not pass through the dialysis bag. Since the solutions remaining in the bags were not filtered or centrifuged before making color

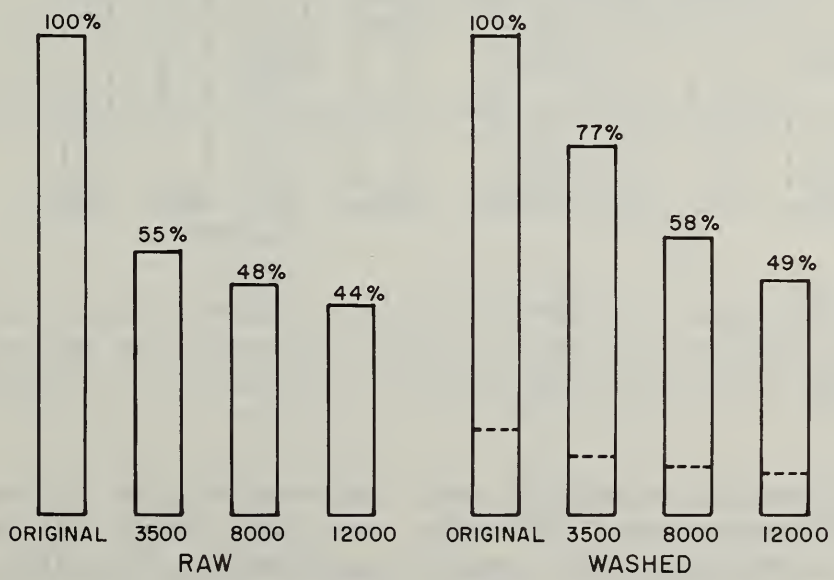

Fig. 1A. Percentages of color retained in dialysis bags, sugar No. 1. Area beneath the broken lines represents the percentages of color based upon the original color in the raw sugar.

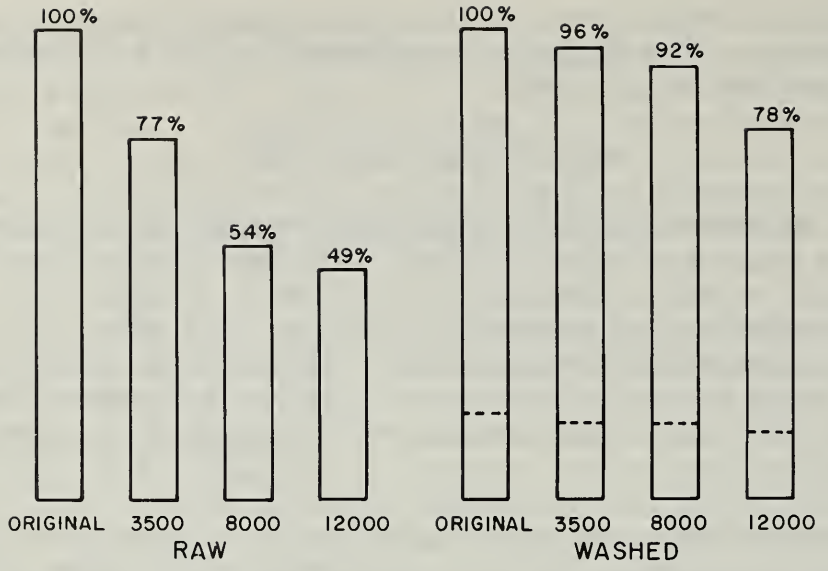

Fig. 1B. Percentages of color retained in dialysis bags, sugar No. 2. Area beneath the broken lines represents the percentage of color based on the original color in the raw sugar.

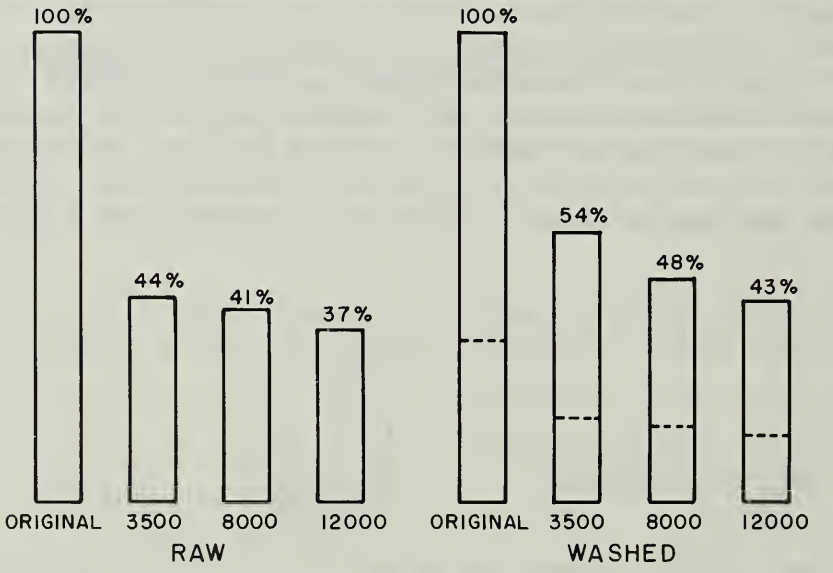

Fig. 1C. Percentages of color retained in dialysis bags, sugar No. 3. Area beneath the broken lines represents the percentages of color based upon the original color in the raw sugar.

measurements the turbidity should be about the same as that in the solution when the original color measurements were made, and there should not be any difference in the color measurement that could be ascribed to turbidity change.

The weights of the nondialyzable material retained in each of the different M.W. cutoff bags are shown in Table II. The data in Table II is shown graphically in Figures 2A, 2B, 2C, and 2D. It is interesting to note that 56% to 88%

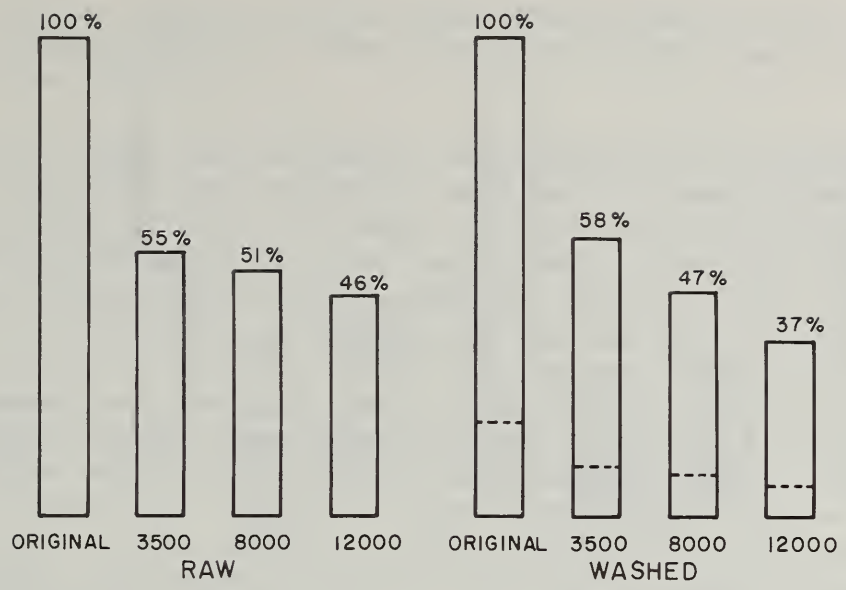

Fig. 1D. Percentages of color retained in dialysis bags, sugar No. 4. Area beneath the broken lines represents the percentages of color based upon the original color in the raw sugar.

Table II

Weight of nondialyzable material retained in dialysis bags of 3,500, 8,000, and 12,000 molecular weight cutoff.

Sugar No.	Wt. nondialyzable material retained in bag, g/100 g sugar, molecular weight cutoff		
	3,500	8,000	12,000
1. raw	0.23	0.18	0.13
washed	0.10	0.09	0.08
2. raw	0.33	0.28	0.24
washed	0.10	0.09	0.06
3. raw	0.27	0.25	0.24
washed	0.07	0.07	0.06
4. raw	0.21	0.17	0.17
washed	0.06	0.06	0.05

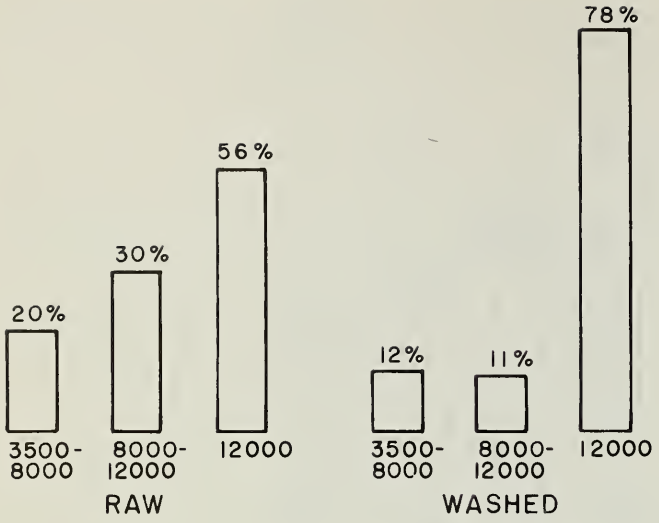

Fig. 2A. Weight distribution of non-dialyzable material, sugar No. 1.

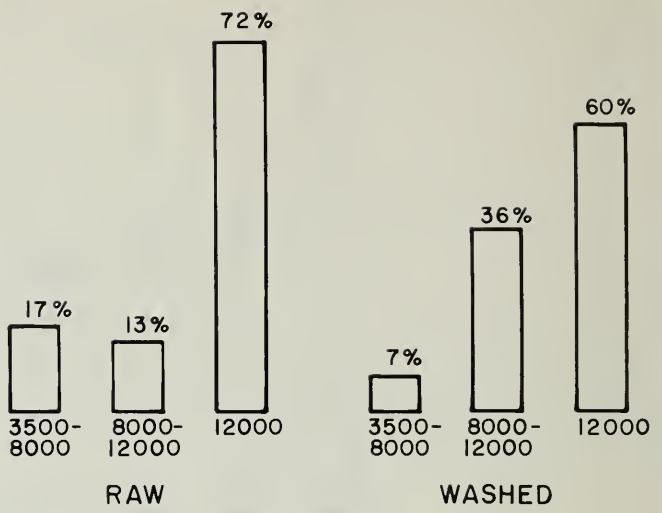

Fig. 2B. Weight distribution of non-dialyzable material, sugar No. 2.

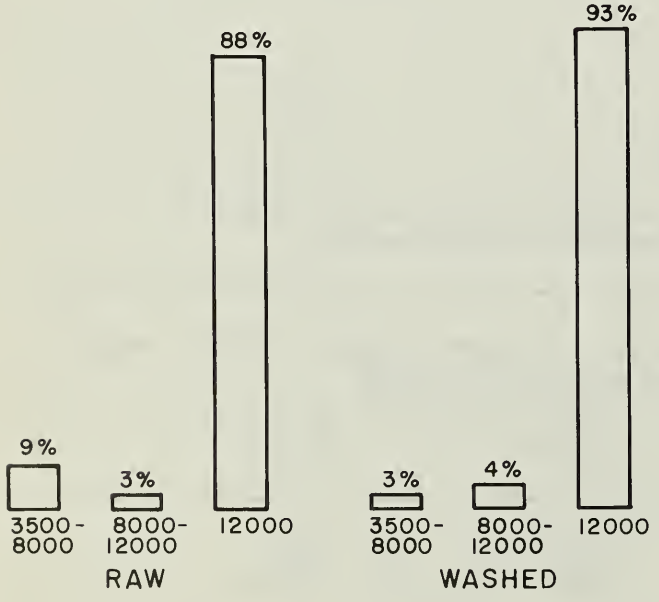

Fig. 2C. Weight distribution of non-dialyzable material, sugar No. 3.

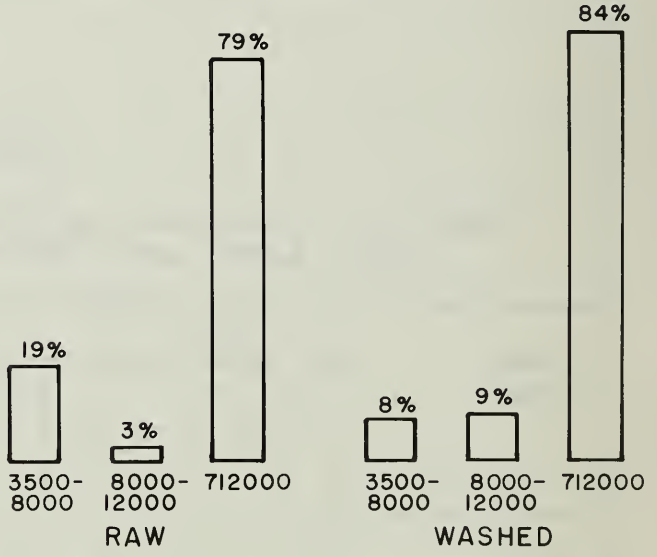

Fig. 2D. Weight distribution of non-dialyzable material, sugar No. 4.

of the nondialyzable material in the raw sugar was of molecular weight greater than 12,000 while that in the washed sugar ranged from 60% to 93%. This again indicates that washed sugar contains a slightly higher percentage of high molecular weight material than does raw sugar.

The fluorescent compounds released by mild hydrolysis of the nondialyzable material in sugar are apparently the same as or similar to the plant pigments reported by Farber and Carpenter (2). Ferulic acid, caffeic acid, and sinapic acid were positively identified by comparison of mobilities and spot enhancement

with authentic samples on high voltage paper electrophoresis and thin layer chromatography. Ferulic acid has been identified in the pentosans from wheat (13) and rice (14).

These phenolic acids and flavonoids are apparently attached to the ISP by ester linkages since they are removed by mild acid or base hydrolysis. They are not glucoside linkages because glucosides are not hydrolyzed under basic conditions. These ester linkages may occur in two ways: the carboxyl group of the phelolic acid may form esters with the hydroxyl groups of the ISP; or, the carboxyl groups of the glucuronic acid units of the ISP may be esterified by the hydroxyl groups on the phenolic acids or flavonoids. The latter may account for the heretofore anomalous fact that some sugars do not form acid beverage floc, even though they contain the necessary ISP and protein; the reason could be that the carboxyl groups are not available to form coacervates with the proteins because they are esterified. We have found that a floc-negative sugar will become floc-positive by the addition of the mildly hydrolyzed nondialyzable material from sugar. The carboxyl groups are freed by mild hydrolysis to enter into coacervate formation.

The substituted ISP is in colloidal suspension at room temperature but is soluble in sugar solutions at refinery operating temperatures and consequently is not removed by clarification and filtration. The free phenol groups on the ISP substituents may then become oxidized or react with iron further along in the process to form darkly colored compounds of high molecular weight such as have been isolated by dialysis in this study. These ISP derivatives no doubt account for some of the turbidity and much of the fluorescence in sugar solutions.

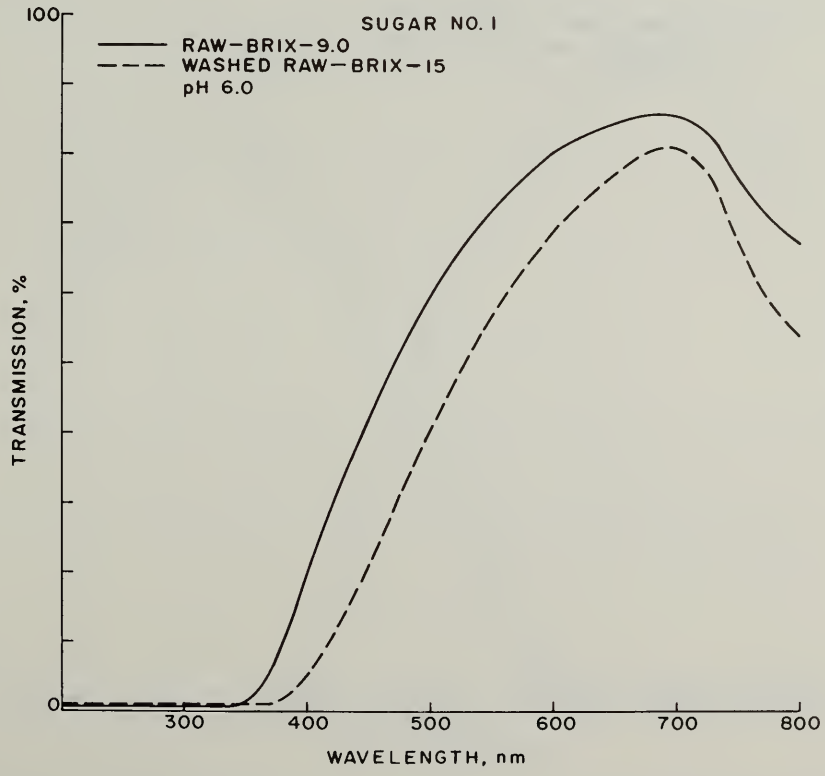

Fig. 3. Absorption spectra of raw sugar No. 1 before and after washing (pH 6.0).

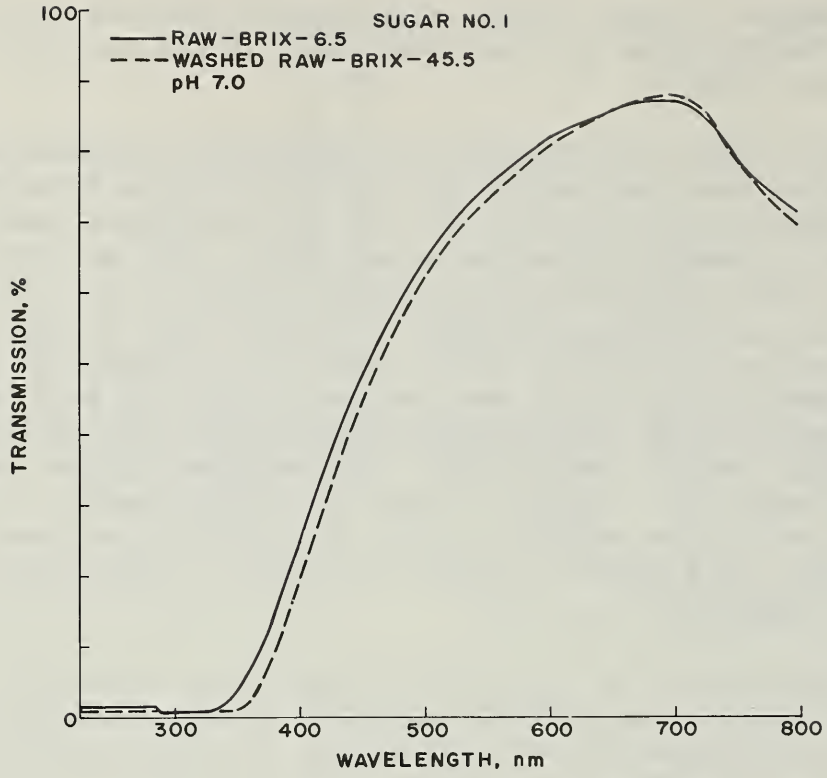

Fig. 4. Absorption spectra of raw sugar No. 1 before and after washing (pH 7.0).

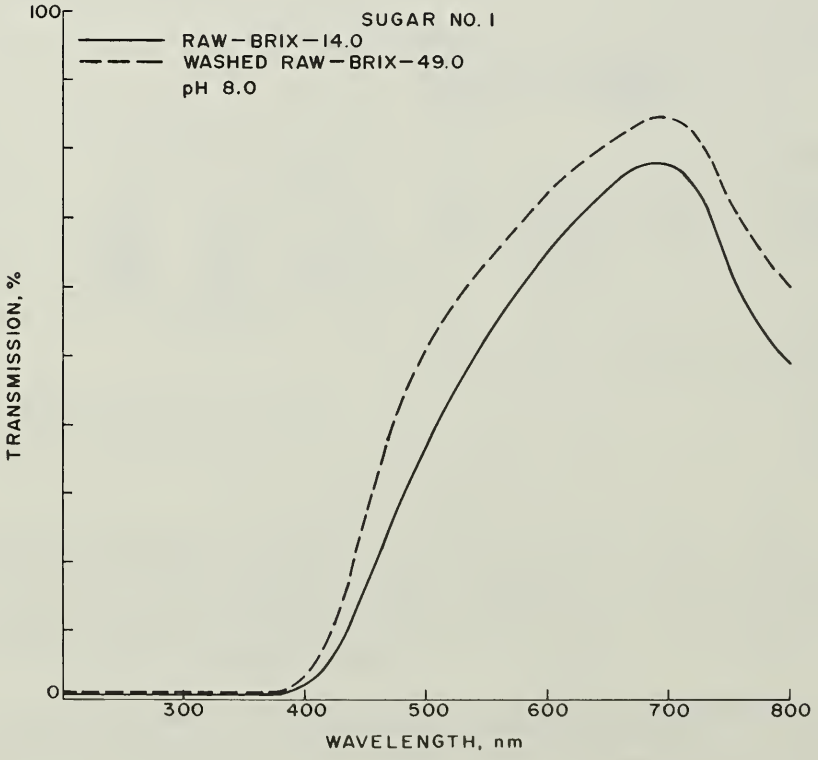

Fig. 5. Absorption spectra of raw sugar No. 1 before and after washing (pH 8.0).

It was found that washed sugar color contains a greater percentage of high molecular weight colorants than raw sugar. It was therefore of interest to determine if there were differences in the optical properties of raw and washed sugar colors. Figures 3, 4, 5, 6, 7, and 8 show the absorption spectra of two samples of raw sugar before and after being washed. The spectra were made from 300 nm to 800 nm at pH values of 6.0, 7.0, and 8.0. These figures show no difference in the optical properties of the total sugar color in raw and washed sugar between pH 6.0 and 8.0. This does not exclude the possibility of differences in various fractions of the color.

CONCLUSIONS

It has been shown that washed sugar contains a greater relative percentage of high molecular weight colorant than raw sugar. This is also true in the case of nondialyzable material (i.e. high molecular weight solubles and insolubles) in washed sugar compared to raw sugar. It has also been shown that mild hydrolysis of the nondialyzable material in sugar yields polyphenolic acids. These compounds are probably attached to the ISP by ester linkages.

It was also shown that even though washed raw sugar contains higher molecular weight colorants than raw sugar, there is no apparent difference in the ultraviolet and visible spectra of the whole sugar color. Since no differences were found in the spectra of raw sugar and washed raw sugar it may be assumed that the high molecular weight colorants have the same absorption as the low molecular weight colorants, or, alternatively, that strongly absorbing moieties in both high and low molecular weight compounds swamp out other differences in the spectra.

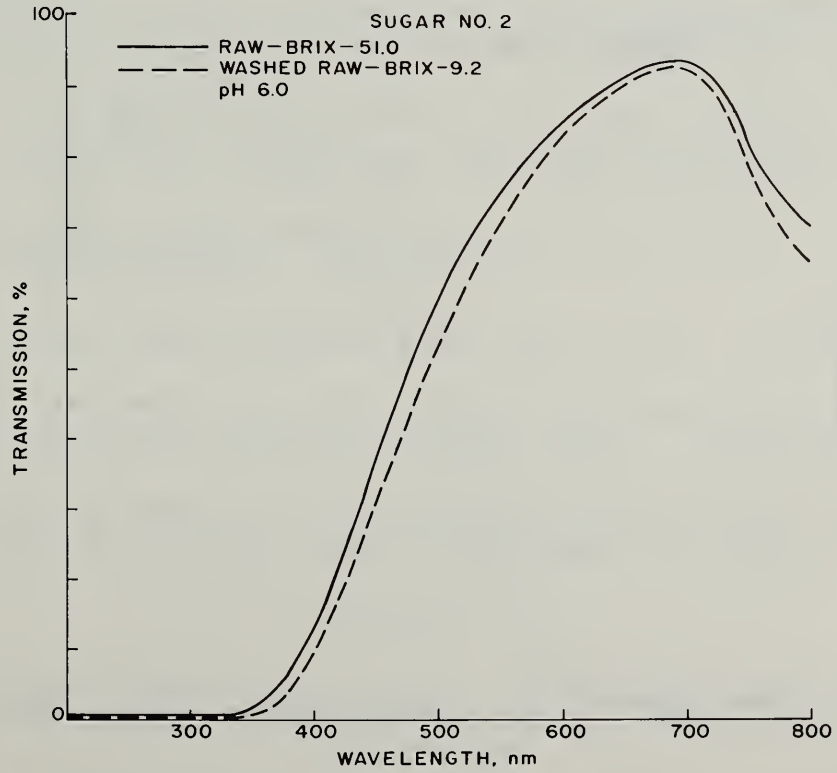

Fig. 6. Absorption spectra of raw sugar No. 2 before and after washing (pH 6.0).

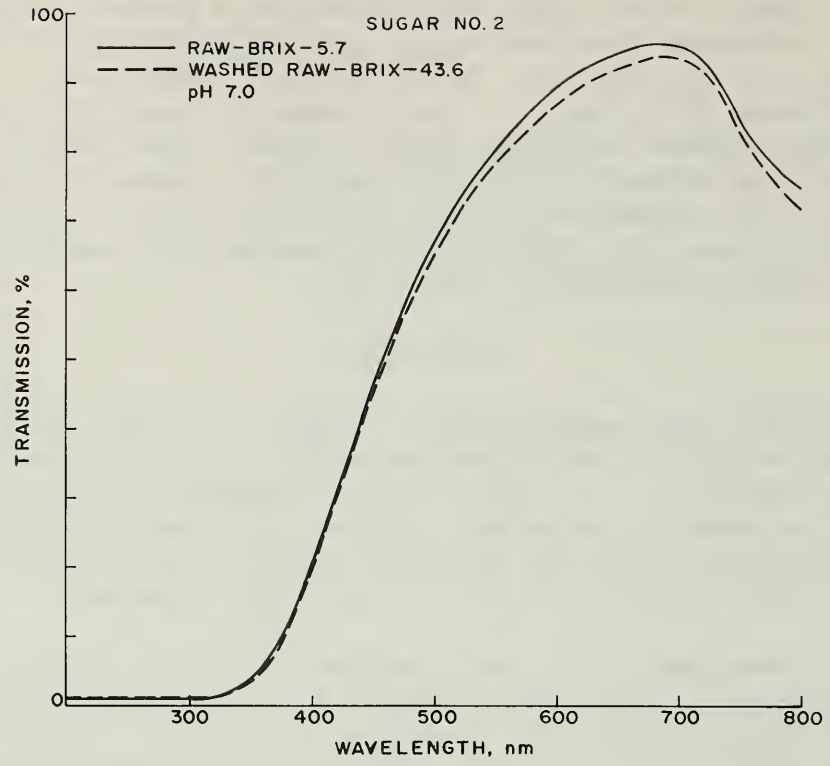

Fig. 7. Absorption spectra of raw sugar No. 2 before and after washing (pH 7.0).

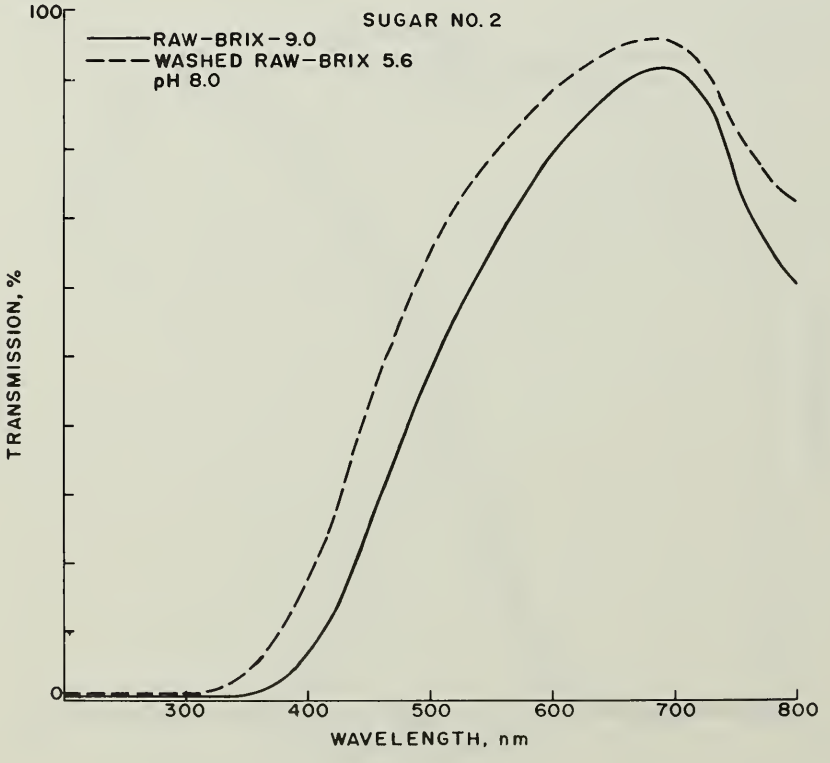

Fig. 8. Absorption spectra of raw sugar No. 2 before and after washing (pH 8.0).

Since the high molecular weight colorant compounds appear to be included selectively in the sugar crystal, it is these compounds that require further identification so that they may be removed during refining to allow more efficient crystallization of sugars of low color.

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DISCUSSION

R. K. Sinha (Activated Carbon Div. Calgon): Did you look into the functional groups of the color bodies? What parts are acidic, neutral, and basic?

E. J. Roberts: No, we did not do that. That is extremely difficult to do. If you try to do much on the basic side, acids are produced. If you work on the

acid side, more acids will be produced so you are almost blocked. There have been studies made on the acidic properties of the colorants.[1/]

R. K. Sinha: Are there any other causes of floc formation besides the polysaccharide reacting with protein at low pH?

E. J. Roberts: Yes, there are other types of floc. There are microbiological products which resemble acid beverage floc. Things that are in the water sometimes will cause floc-like formations. The acid beverage floc that we are talking about can be distinguished from other types when you examine it carefully. The others look like a ball of cotton, or stringy web-like material. Acid beverage floc looks more granular, and will dissipate upon agitation.

R. K. Sinha: Are inorganic ions responsible for the floc?

E. J. Roberts: No. Inorganic ions have no effect, except silicate. Addition of silicate will sometimes make a floc more visible, but as far as we know it will not of itself cause floc. When the floc forms, the polysaccharide which is negatively charged interacts with the positively changed protein to form small particles. As these particles coalesce they gather up the other collodial materials like silica, starch, wax, and lipids forming larger and larger particles until the floc will settle out. If there are not enough of these other collodial materials present, it may be that the floc will form but if it happens to have the same refractive index as the solution, it will not be visible. If other colloidal materials are present to change its refractive index then it will become visible. Soluble silicate is the only inorangic compound that was found to influence floc formation or visibility.

T. N. Pearson (Imperial): When you were comparing the raw sugar with the washed raw, how many different countries of origin did you examine? I think that by examining raws of different origins you will find a change in your results due to the way the raws are processed at the mills.

E. J. Roberts: We examined four different origins.

M. C. Bennett (Tate & Lyle): I think that the country of origin is not so important as is the history of how the raw sugar was made. There are quite wide differences in technique in the raw sugar house. There are different ways of boiling the A strike raws depending upon whether you have brought your C through B to A, as in the Double Einwurf System or, whether, as the South Africans do, you remelt all C's and B's and make raw sugar only from A's. Because you see you can get layer formation inside the raw sugar crystal. This would have a tremendous bearing on the sort of analysis that you were doing. Maybe you have to go back to known raw sugar factories, and pinpoint the precise boiling sequence followed in that raw factory.

E. J. Roberts: That is a good suggestion. Perhaps if we knew the exact boiling sequence we would have found a significant effect in some types of boiling schemes.

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TECHNIQUES FOR THE ISOLATION OF CANE SUGAR COLORANTS

by

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ABSTRACT

Methods are described for the separation of mill syrup colour from sugar to yield "solid colour". The latter is further fractionated by gel permeation and polyamide column chromatography to produce fractions sufficiently enriched in a single colour component for final purification by paper chromatography. A major cane sugar colorant, tricin-7-glucosylglucoside was isolated from mill syrup using these techniques.

Application of these procedures paves the way for the study of the properties of single colour components and their quantification by analytical techniques such as high performance liquid chromatography.

INTRODUCTION

Two of the main functions in milling and refining are to remove coloured impurities and to recover sucrose. A knowledge of the composition of colour can lead to the development of more efficient ways of removing it. Coloured impurities in cane sugar products are present in trace quantities. Before any studies of their composition or quantification can proceed, methods are required to separate sufficient amounts of them from sugar. This requirement was recognised as early as 1945 by Maclaren[1] in his initial colour studies.

In this paper we describe procedures used by us to:-

(a) separate colorants from sugar and salts and concentrate them,
(b) fractionate the colour concentrates from (a) and
(c) isolate and purify individual compounds from the colour fractions in (b).

We illustrate this in the recovery of tricin 7-glucosylglucoside from a mill syrup. The location of this pigment on a 2-D thin layer chromatogram (TLC) of mill syrup colorants is shown in Figure 1.

EXPERIMENTAL

Three methods have been commonly used to separate colorants or related pigments from sugar or carbohydrate solutions. All have the following deficiencies.

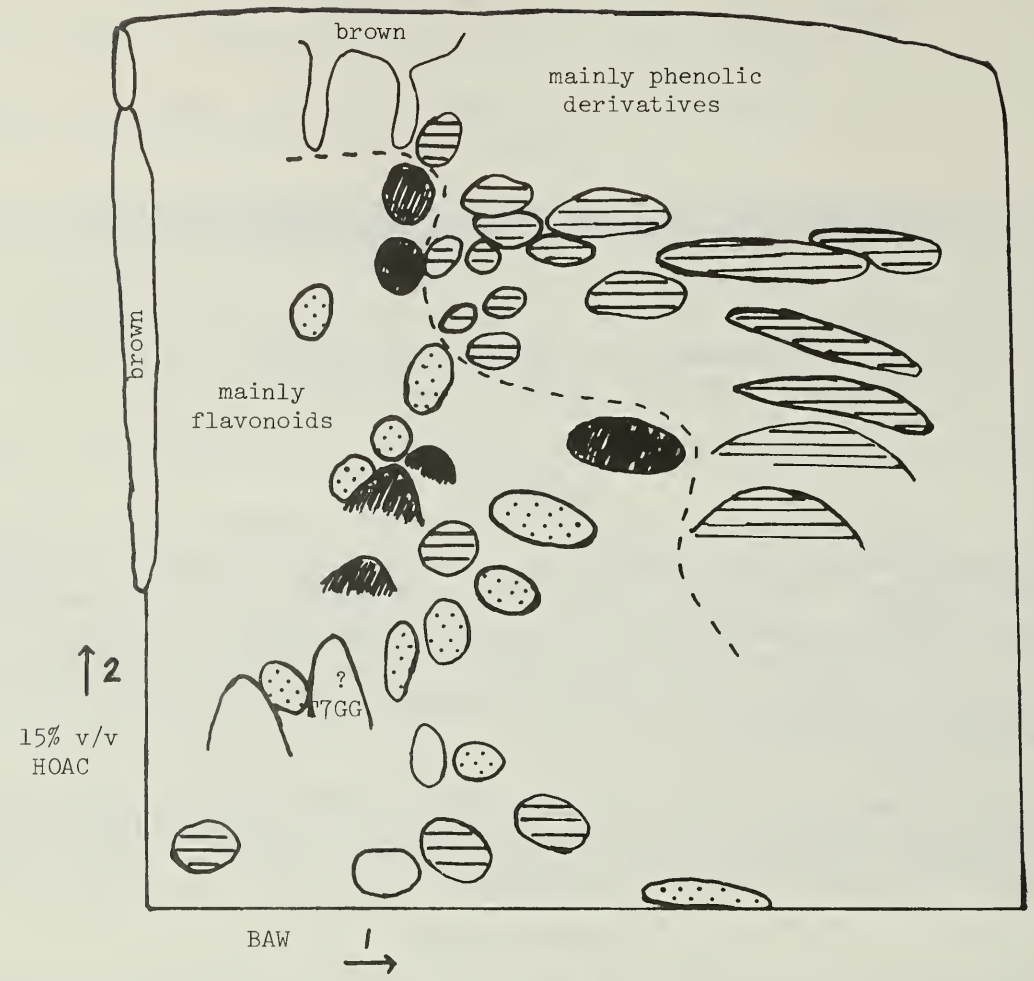

Figure 1. Thin layer chromatogram of mill syrup colorants.

Recovery of colorants by activated carbon adsorption[2] and ethyl acetate solvent extraction[3] are not quantitative. Separation of colour from granulated sugars and other light coloured products by alcohol precipitation becomes impractical because of the copious amounts of alcohol required in processing them by this technique.

Recently, N H Smith[4] reported another technique for recovering cane sugar colorants using a polymeric adsorbent resin (Amberlite XAD-2). Smith diluted and acidified sugar solutions prior to passing them over the resin bed. After sample loading was complete the resin was washed free of residual sugar with distilled water. The adsorbed colorants were recovered by extraction with methanol. Smith did not report his data on colorant recovery with methanol,

however the technique offered sufficient promise for us to assess XAD-2 resin for quantitative recovery of colorants.

Recovery of Cane Sugar Colorants by XAD-2 Resin

Properties of XAD-2 Resins - Analytical Applications

XAD-2 resin is an insoluble cross-linked polystyrene polymer supplied by Rohm and Haas (R&H) in the form of 20-50# beads[5]. This adsorbent was initially developed by R&H for water pollution control. However, its application is increasing in trace analytical chemistry. For example, it is used as an "accumulator" resin to selectively adsorb trace organic compounds from industrial effluents[5] or active ingredients[6] in cough mixtures from the bulk syrup.

Colorant Recovery Method

We used spent regenerant to find optimum conditions for recovery of colour by XAD-2 resin. Spent regenerant is a brine solution of sugar colorants desorbed from strong base anion exchange resins used for decolorising raw liquor in one of our refineries. The colour of the solution was 12.9 (A420nm, 1cm, pH9). A bed volume (BV) of 200ml of resin was found to be more than adequate to adsorb the colorants present in 40ml aliquots of this solution.

(a) Sample pH. Sample solutions were acidified to pH 3 with concentrated hydrochloric acid. This suppressed the ionisation of the colorants which would have inhibited their adsorption on the resin.

(b) Sample loading. Acidified sample solutions were loaded on the resin columns (BV=200ml) at the rate of 130-150ml/hr. Flow rates recommended by R&H[5] for decolorising raw sugar solutions were five times greater and would have resulted in colour breakthrough if used in the recovery tests. Flow rate was controlled by Halu stop-cocks with needle valves fitted to the exits of the columns. Solutions to the columns were fed under gravity.

(c) Salt removal. Before any colorant desorption from the resin could proceed, residual salt on the resin bed was removed by washing with a minimum 2BV of distilled water. In practice, it was preferable to irrigate the column overnight with distilled water. The same flow rates were used as in sample loading.

(d) Colorant desorption. Colorant recovery was found to be less than 90% on a colour attentuation basis when methanol extraction was used. Recovery was increased to 95% when the elution cycle consisted of 1BV of 4% v/v ammonium hydroxide solution followed by 2BV of methanol. Lower recoveries were obtained when the resin bed was used more than four times.

The elution rate was the same as that for loading. The desorbed solution of colorants was concentrated under vacuum at 38°C to remove ammonia and methanol. Colorants in the solid form were obtained when the concentrated colour solution was freeze dried.

Application of Colorant Recovery Method to Cane Sugar Products

After optimising the XAD-2 colorant recovery technique with trials on spent regenerant we applied it to cane sugar products. Sample solutions were diluted with distilled water to 20°Bx or less as the resin bed broke up and floated on top of more concentrated sugar solutions. The samples were processed on XAD-2 resin in the same manner as spent regenerant.

Mill syrup. In developing a method for isolating cane sugar colorants, it was necessary to have an adequate supply of colorants for fractionation by large scale gel permeation. Gram quantities of solid colour were recovered from mill syrup (A420nm, 1cm, pH9=50) with XAD-2 resin. From 100g solids of mill syrup a yield of 1g of "colour" was obtained after processing on a 200ml bed of XAD-2 resin. We stress that this "solid colour" contains some organically bound ash components, exemplified by such cane sugar colorants as tricin 7-glucoside sulphate.

Fractionation of "Solid Colour" by Large Scale Gel Permeation

The separation of mill syrup colorants was done on a molecular basis using cross-linked dextran gels (Pharmacia Sephadex grade LH-20). Conventional gel fractionation of coloured sugar solutions yields 3 or 4 fractions. By using a desugared solution of mill syrup colour and modifying the gel permeation elution techniques, it was possible to enhance colour fractionation considerably.

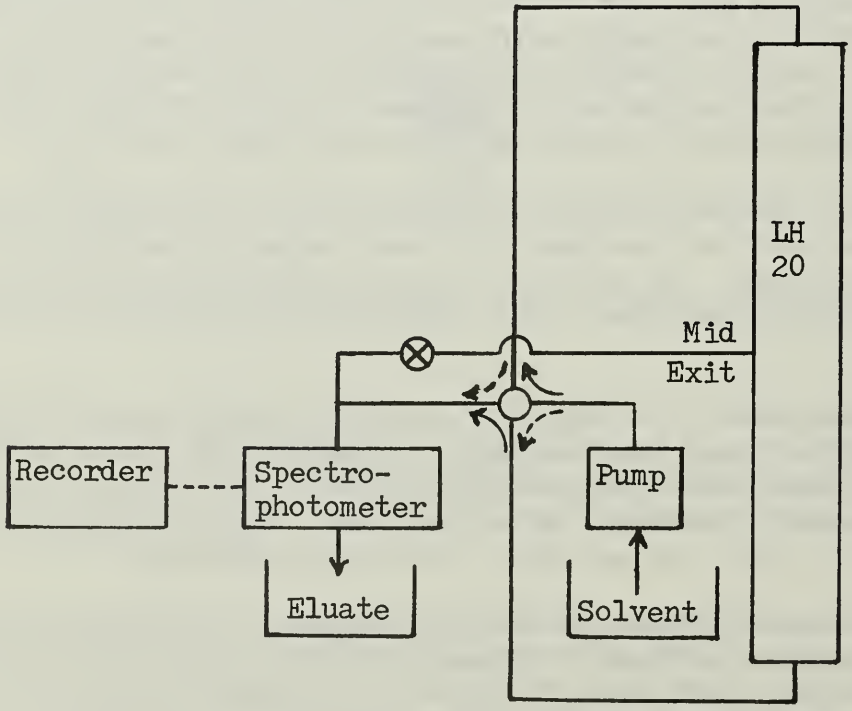

Figure 2. Flow diagram of large scale gel permeation apparatus.

Equipment

The chromatography column was made from a Quickfit glass pipe 80cm in length and 5cm in diameter. Both ends of the column were sealed with Pharmacia adjustable pistons. Other equipment included a solvent pump which was connected to both ends of the column by a 4-way stop cock. Colorants eluted from the column were monitored by a spectrophotometer (with 0.5cm flow through cell) in series with a recorder. The flow diagram of the equipment is shown in Figure 2. It shows schematically the arrangement required to effect this reverse flow system. The symmetrical construction of the column and the use of a 4-way stop cock permits descending or ascending chromatography by just a 90^{o} turn of the stop cock.

The equipment was housed in a room which could be darkened. The colour fractions on the column were detected with a 60cm UV fluorescent lamp. The latter was clamped upright close to the column and emitted light at 350nm. The lamp was masked in such a way as to leave only a 0.5cm longitudinal slit through which the UV light emerged. The resultant narrow beam of near-UV light was extremely helpful in revealing most of the bands of colour separated on the column.

Column Preparation

The column was filled with sufficient Sephadex LH-20 in the form of a slurry to occupy a settled volume of 1500ml in water. After settling, the top piston was adjusted to ensure that solvent distribution was in close contact with the surface of the gel.

Sample Preparation

Solid mill syrup colorants (500mg) were dissolved in 40ml distilled water. On acidifying the aqueous solution with a drop of concentrated hydrochloric acid, some polymeric colour was precipitated. This was removed by centrifugation leaving a supernatant solution containing 430mg of colour. Removal of the precipitated colour prior to gel filtration of the sample was necessary as its presence in earlier experiments interfered with fractionation of other colorants on the column.

Operation

The colorant solution was pumped on to the top of the column at a flow rate of 100ml/hr. After sample loading, the flow rate was doubled for elution with the solvents. Complete removal of the colorant compounds from the column was brought about by the use of the following sequence of solvents:-

a) distilled water
b) 20% aqueous solution of methanol
c) 40% aqueous solution of methanol
d) a solvent gradient having 40% methanol in the main feed vessel and 0.1 M NH_3 in 40% methanol in the secondary.

The effluent after being fed through the flow-through cell in the spectrophotometer was collected in a measuring cylinder. The spectrophotometer, which had a digital read-out, was operated at 350nm using a tungsten lamp.

Thus, during fractionation of the colorants, it was possible to observe the colour bands on the column, note changes in absorbance readings of the effluent and study the shape and size of the profiles of the various colorants as they were registered on the recorder. The arrangement provided an early warning system for the imminent arrival of a fresh colorant band in the effluent sample vessel, so that the sample could be changed with minimum overlap of colorants. This reduced the work in the subsequent purification steps of single colour components.

Reverse Flow Techniques

In earlier trials, attempts to collect each colorant band as sharply as possible failed to some degree because each band diffused as it progressed down the column. While shorter columns would have reduced band diffusion, this would be offset by loss in colour separation.

However, it was observed that if the direction of solvent flow were reversed when a band became diffuse in outline, it narrowed to one having well defined boundaries. By careful manipulation of upward and downward flow it was possible to remove fairly clearly defined bands from either the top or bottom of the column.

Since some of the bands seemed to be more clearly defined around the centre of the column an attempt was made to remove them at this location by introducing a centrally positioned outlet. The latter had to be blown into the side of the column very carefully to ensure a smooth undisturbed wall around the exit hole. Any change in contour may well have disrupted the even flow of solvent through the media. Our exit tube incorporated the female portion of a ground glass joint. The male joint had a sintered disc on the extreme inner end such that when inserted in the exit tube it fitted flush with the column wall and prevented loss of the filtration media.

With the normal exit closed, it was possible to remove colorants through this central exit with both up and down flow, but always some portion remained on the column because of the tendency for the solvent to channel into the exit. Thus, if the complete colorant fraction is required, this method of removal is not recommended.

Analysis of Fractions

Twenty-two fractions were collected, the colours of the solutions ranging from very pale yellow to brown. The relevant gel permeation data are given in Table 1. Any methanol or ammonia was removed under vacuum on a rotary evaporator before freeze drying and weighing the fractions. Recovery of colorants loaded on the column was over 95% by weight. The earlier fractions tended to be the largest by weight, while those eluted last were very small. For example, the first three fractions accounted for nearly half of the sample applied to the column.

TABLE 1
GEL PERMEATION DATA (SEPHADEX LH-20) FOR MILL SYRUP

FN	SOLVENT	FLOW DIRECTION	COMPOSITION			
			Polymeric	Phenolic Derivatives	Flavonoid	
					Tricins	Others
1	Distilled Water	Down	+			
2	"	"	+			
3	"	"	+	+		
4	"	"		+	+	
5	"	"		+	+	
6	"	"		+	+	+
7	"	"		+	+	+
8	Methanol (20%)	"		+		+
9	"	"		+		+
10	Methanol (40%)	"		+		+
11	"	"		+		+
12	"	"		+		+
13	"	"		+		+
14	NH_3/Methanol	"		+		+
15	"	Up				+
16	"	"				+
17	"	Up/Side Exit				+
18	"	Up				+
19	"	Up/Side Exit				+
20	"	Up				+
21	"	"				+
22	"	"				+

Each fraction was analysed for flavonoids and other phenolic derivatives by two dimensional TLC. We used 10cm square microcrystalline cellulose plates and the solvents BAW (n-butanol:acetic acid:water 4:1:5 upper phase) and 15% v/v acetic acid. The plates were examined in UV light (350nm), after fuming with ammonia and after spraying with 10% w/v sodium carbonate solution. Many phenolic derivatives turn shades of blue or green with ammonia or sodium carbonate while flavonoids change to yellow or mustard. Colorants which did not absorb in the UV were seen on the plate in visible light. Tracings were made of the spots detected in each chromatogram.

The composition of each fraction is outlined in Table 1. More than 20 phenolic derivatives and 50 flavonoids were detected altogether. Some fractions appeared to have phenolic derivatives and a dominant flavonoid. We suspected that these flavonoids were the same as found in Saccharum officinarum[7]. The isolation and purification of one flavonoid, tricin-7-diglucoside (T-7GG), is described.

Isolation and Purification of Individual Colour Components

Column chromatography is probably the most useful technique for the isolation of large quantities, i.e. several mg, of flavonoids from plant extracts. The best adsorbent for the separation of all types of flavonoids is polyamide because of its high capacity and resolution. Mixtures of water and methanol are suitable eluants for the separation of flavone glycosides and these compounds are known to be present in the Saccharum plant. We applied the methods for plant flavonoids, described in "The Systematic Identification of Flavonoids"[2] to our cane sugar colorants.

Preparation of Polyamide Column

Polyclar AT was sieved through 100 and 200# sieves and the fraction -100 +200# was retained. The polyamide was washed with water, then 50% v/v aqueous methanol and again with water. Sufficient aqueous slurry of polyamide was poured into a column (dia. 2cm x 35cm) to half fill it. The base of the column was plugged with a small amount of glass wool and the exit fitted with narrow nylon tubing clamped by a screw clip. Excess water was drained off quickly to assist settling and a layer of sand placed on top of the column.

As in the gel permeation separation, the column was placed in a room which could be darkened for UV detection of separated colour components.

Separation of Tricin Derivative

Fraction 6 (43mg), containing the suspected tricin-7-glucosylglycoside (T-7GG), was dissolved in a small amount of water and applied to the top of the column with a Pasteur pipette. The column was eluted with water under gravity at 20-25ml/hr. Several bands became apparent in UV light. These were dark grey, pale green, orange-yellow, brown and blue. Fractions corresponding to these bands were collected. When no more bands were observed the column was eluted with 50% v/v methanol to check that elution was complete.

The fractions were freeze dried as previously. Total recoveries approached 95% by weight. The fractions were analysed by 2D thin layer chromatography using the solvent system described above. Smaller plates, 6.5cm square, were found to be satisfactory for these runs.

The general elution pattern from the polyamide column was similar to that from the gel fractionation in that phenolic derivatives were eluted before flavonoids. As a result of separation and concentration, more compounds were detected in the fractions than had been apparent in the starting material. One fraction corresponding to the orange-yellow band yielded a "dirty" green-yellow solid (12mg) after freeze drying. This fraction on analysis contained the suspected tricin derivative (T-7GG) with other minor flavonoids.

Cellulose was recommended as a medium for further purification[8]. Trials with small cellulose TLC plates using dilute acetic acid as a solvent indicated that this approach was promising. However separations attempted on cellulose columns were unsuccessful.

This being the case, the material was further purified by dissolving it in a minimum of distilled water and passing it over a fresh polyamide column of similar dimensions to that used in the first purification run. A bright yellow-green solid (4mg) was obtained. This was less than 1% of the total colour solids applied in the primary separation of the mill syrup colorants by gel filtration. On analysis by TLC this solid was mainly the tricin compound with two minor compounds. Final purification was achieved by paper chromatography using BAW as a solvent.

The chromatographically pure compound had the same Rf values in four solvents as T-7GG which had been isolated from the leaves of a Saccharum officinarum clone.

DISCUSSION AND CONCLUSIONS

Three column chromatography procedures were used in series to recover a flavonoid colour component from mill syrup. Final purification was effected by paper chromatography. The pure colour compound was identified as tricin 7-glucosylglucoside. The latter, which is a major colour component of mill syrup accounted for a small fraction of the weight of the total colour solids used in the colour fractionation.

Removal of sugar from the mill syrup sample by the first column method (XAD-2 colour concentration), improved the separation of colour into molecular fractions by the second column procedure (Sephadex LH-20 gel permeation). Elimination of polymeric and other factory colorants by acid precipitation and gel permeation enhanced the subsequent separation of the colorant molecular fractions on polyamide columns.

Recovery of colour from XAD-2 resin was over 95% on an absorbance basis and recovery of solid colour from gel permeation and polyamide columns approached 95% by weight.

Mill syrup colour was a most complex mixture but was comparatively rich in low molecular weight colorants. Many of the molecular colorant fractions were too small to proceed with further separation of the components.

Preliminary studies of colorants in refinery products indicate that these are less complex mixtures and would require different elution procedures for their isolation. Nevertheless, the experience gained in the present investigation will prove valuable when we attempt the recovery and purification of colour components from white sugar and other refinery products.

The techniques described make it possible to isolate individual colorants in the solid form from cane sugar products. Thus, the way is now open for the study of properties of single colour components and their quantification by techniques such as high performance liquid chromatography.

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DISCUSSION

E. J. Roberts (CSRRP): Sugar colorants are very fragile, and since strong salt solutions will often break up hydrogen bonding, I wonder what effect the brine had on the colorants. Also, operation at pH 3 will in some cases hydrolyze the polyphenolic acids off of polysaccharide moieties. Also, operation in 4% ammonia may effect the characteristics of the colorant by an alkaline hydrolysis.

P. Smith et al: Our experience with refinery colorants indicates that salt has had very little effect on their structure. We have observed that the same spectrum of colorants is present in feed liquors for our factory ion exchange resins and in the brine solutions recovered after regeneration. We concede that brine, lime and ammonia would alter the structure of raw cane juice colorants. For example, mill clarification results in the alkaline degradation of cane juice colorants. This produces new colorant species. In essence, when we examine post-clarification colorants we are observing the chemical "debris" of alkaline degradation processes. The surviving colorants would be expected to be alkaline stable.

On the question of low pH affecting colorants we have the opposite effect. In attempting to determine the structure of some colorants such as flavonoid glycosides we found that the latter required prolonged heating with hydrochloric acid for hydrolysis. Some times we fail to release the sugar. However, Dr. Robert's comments on low pH would be relevant to untreated cane juice colour.

F. G. Carpenter (CSRRP): I might add that even the relatively high concentration of methanol might alter the colorants from what they were originally in the juice to something less complex. I don't visualize them making new colorants, but they might break up into less complex combinations.

P. Smith et al: The only way we can be sure that our isolation techniques do not alter the structure of the colorants, is to subject the purified colorants to the same recovery procedures and check the breakdown products. We believe that those colorants with olefinic bonds and ring structures must undergo isomerisation. However, the ratio or the isomers will be determined by the equilibrium constants. Undoubtedly, a change in solvent systems such as an increase in methanol will alter the equilibrium constants and hence the ratio of isomers.

DEXTRAN PROBLEMS IN SUGAR PRODUCTION

by

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ABSTRACT

Dextran, composed of α-1,6 linked polymer glucose sequences, is a major problem in the manufacture and refining of sugar from sugarcane. Dextran problems are primarily the result of processing partially deteriorated cane, but they can also be the result of poor housekeeping during processing. Refineries not only receive dextran occluded within the sugar crystal, that cannot be removed by affination, but they also recirculate large quantities of sweetwaters that are good media for dextran development. These problems are discussed, and selected data are included to show the magnitude of the dextran problem at several processing steps.

INTRODUCTION

Dextran is the name assigned to a family of polysaccharides that is seldom found in the healthy sugarcane plant, but which can grow rapidly in damaged cane, before and after harvest, through bacterial contamination. Dextran formation continues to be a problem throughout the manufacture of raw sugar and in refinery operations. An excellent review of published works on dextran formation and problems in the sugarcane industry was published by Imrie and Tilbury (6).

Molecular Configuration

Dextrans are polymers of glucose (glucans), joined by α-1,6 linkages, and with α-1,4 or α-1,3 linkages at branching points. At least 50% to 60% of the linkage must be α-1,6 to define a dextran. The degree of branching depends on the strain of bacteria that produced any particular dextran (10), and the diversity of dextrans is due to these structural differences. Physical properties depend in part on the extent of branching (13). Figure 1

**Cane Sugar Refining Research Project, Inc.

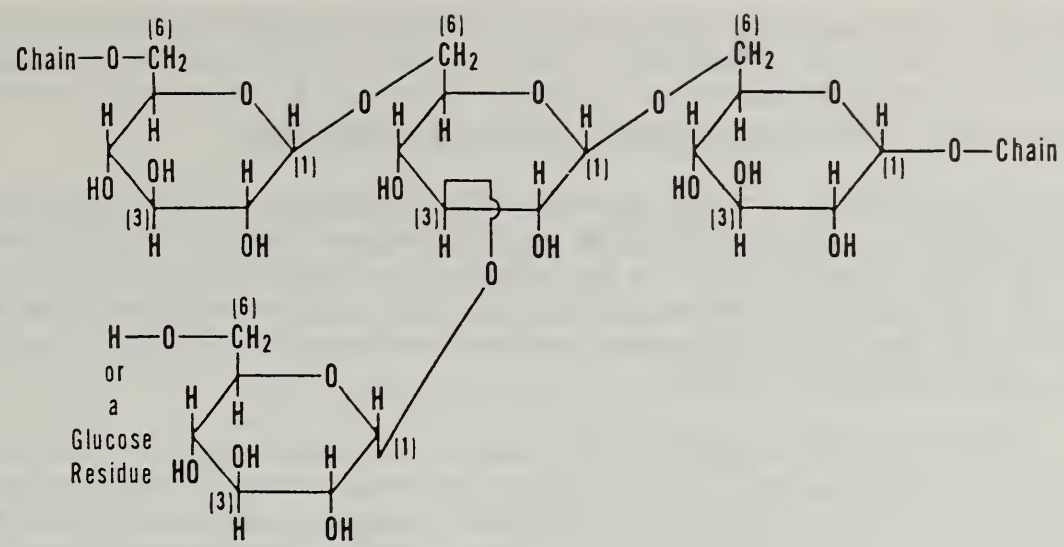

Figure 1. Molecular structure of a typical dextran molecule.

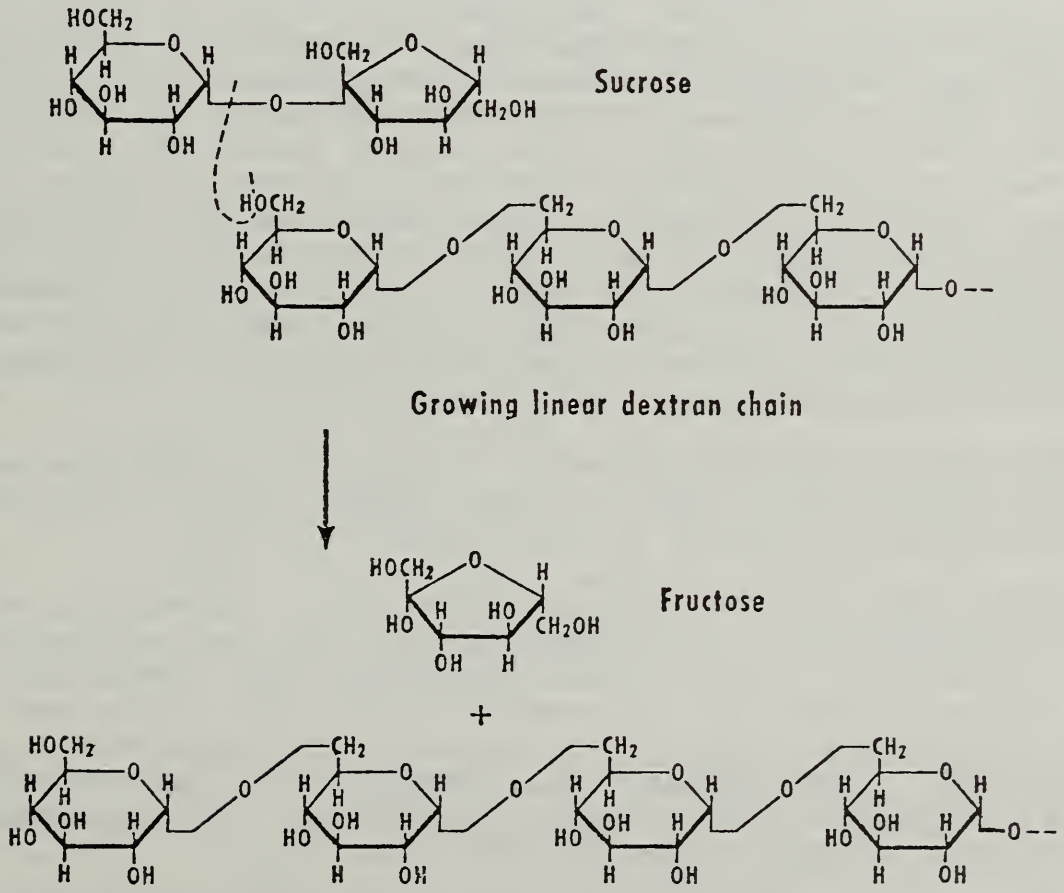

Figure 2. Synthesis of dextran by dextransucrase enzyme.

shows the molecular structure of a typical dextran molecule (9). From this it can be seen that upon hydrolysis, dextran will yield glucose, isomaltose from the 1-6 linked glucose units, maltose from the 1,4 branching points, or oligosaccharides, depending upon the degree of hydrolysis.

Dextrans are highly dextrorotatory, thus causing problems in polarisation measurements. Their molecular weight ranges from 10^5 to 10^7 and upwards. They are usually soluble in water (the higher the proportion of 1,6 linkages, the greater the solubility) but insoluble in 50% ethanol: this property is the basis for some dextran analyses. Solubility varies, of course, with molecular weight.

There is considerable variety in dextran structure, in the degree and the nature of branching, and in the molecular weight range. This variety exists because of the way dextran is formed: several different kinds of bacteria, and many different strains of those kinds, produce dextran, with each strain producing its own uniquely structured dextran molecule. Among the dextrans that are found in sugar processing, the differences in structure appear to have little effect on the problems they cause in sugar solutions.

Sources and Formation of Dextrans

Dextran is produced, in sugar solutions, by the bacteria Leuconostoc mesenteroides and, less commonly, by Leuconostoc dextranicum (also, although not in sugar solutions, by L. citrovorus) which belongs to the family Lactobacillaceae, tribe Streptococceae. These bacteria contain the enzyme dextransucrase, which synthesises dextran from sucrose, as shown in Figure 2 (8). The greatest difference in structure is shown among dextrans produced by strains of L. mesenteroides: at least ninety-six strains have been identified (10), although not all of these will grow in sugar solutions. Although the various dextrans behave in similar fashion and cause similar problems in sugars, the variations in degree and type of branching and in molecular weight make quantitative analysis difficult and confusing.

Another source of dextran production is the organism Streptococcus mutans, which is found in the human mouth, and there, again through the dextransucrase enzyme, manufactures the dextran that is implicated in caries.

L. mesenteroides is very common in nature, and so contamination with this organism is extremely easy. It is found in most soils, and so is on the cane plant. It is airborne and can contaminate standing water or sugar solutions. The ease of contamination, and the speed with which this organism grows and produces dextran from any source of sucrose make it an ever-present hazard in sugar production. A small infection in a sweetwater line can produce enough dextran in a few days to cause a factory to shut down. L. mesenteroides will not, however, grow at temperatures over 50°C (12).

When mechanical failure in an Australian sugar mill caused a shutdown of 29 hours in duration, the cane stored in the mill yard (chopper-harvested cane) exhibited a 3400% increase in dextran in juice, and the raw sugar produced was "utterly unacceptable in respect to pol, colour, grain size and filterability" (17). The massecuites, with lower-than-normal crystal content, were extremely difficult to purge. In previous experience with deter-

iorated cane, heating surfaces had been fouled with dextrans to the point of no heat transfer.

Dextrans Entry into Sugar Process

Damaged Cane: Cane frequently suffers "natural" damage in the field, before harvest, that allows bacterial infection of the plant. The damage is usually a splitting of the protective rind as the cane matures, or may be the result of storm damage. Certain varieties are more subject to rind splitting than others, and this may explain the unusually high dextran values found, for example, in fresh Jamaican cane where dextran content increases dramatically with cane maturity (6). The most severe rind, or stalk, splitting in cold climate areas is caused by prolonged freezing weather. L. mesenteroides infection can destroy a crop within days under the conditions that favor infestation and dextran production: a freeze followed by warm, wet weather (2). The greatest damage that accelerates dextran formation in cane is inflicted by the burning of standing cane and/or by the mechanical harvesting operations, particularly those associated with chopper harvesters. Rates of cane deterioration are primarily functions of the degree of mechanical damage (4,7), cut-to-crush delay (4,7), environmental conditions (3,4), degree of burn and delay of harvest after burning (1,3,11), and combinations of these factors in conjunction with "natural" damage discussed earlier. In nearly all of these studies, dextran content was the single most important variable considered in evaluating the degree of cane deterioration. Other factors are the drop in pH (or increase in acidity) with related inversion and sucrose loss.

Raw Factory. Since the factory processes cane 24 hours per day, from cane delivered during the daylight hours, it has the problem of managing a storage facility adjacent to the mill. Cane with bacterial contamination deteriorates in storage, and the degree of deterioration can become appreciable during periods of mechanical breakdown or shutdowns for housekeeping and cleanout operations. This problem can be alleviated somewhat by having well managed and modern storage facilities. The time between harvesting and grinding must be as short as possible. Good housekeeping is a must, especially at the mill or thin juice end of the factory, to minimize dextran development during processing. Bactericides are available for application at the mill (6). In spite of precautions, dextran will be formed during the lime clarification of juice where the juice is held for long periods of time. Dextran development in the raw pans, crystallizers and centrifuges is minimal compared to that in the other operations.

Refinery. The dextran load entering the refinery via raw sugar is important in two ways. Dextran has an affinity for occlusion within the sugar crystal, which means that this occluded portion cannot be removed from the raw sugar crystal by affination, and it is processed through the entire system. The portion removed by affination enters further downstream and is recirculated during processing, along with that accumulated from the crystal portion. The study on polysaccharides throughout the refinery process, by Roberts et al. (16), points out how much polysaccharide (including dextran) is recirculated. Dextran formation within the refinery is another problem. The best way to minimize the problem is to maintain strict housekeeping standards at all times, with the optimum use of approved bactericides.

Keeping sweetwater volumes to a minimum will be of particular help, since dextran formation rates in these can be very high during periods of bacterial contamination.

Problems Created by Dextran. Sugar loss is the primary problem. Dextran is formed during the bacterial destruction of sucrose, so that at every location where dextran is formed there will be an equivalent loss of sugar. All other problems are physical in nature, and they are associated with the presence of dextran within the system. In severe cases of infection there can be partial-to-complete blockages of lines, valves and pumps with gelatinous masses of dextran (also known as slime or frog eggs - in Cuba, hueva de rana). Also, the viscosities of massecuites and molasses are a direct function of the amount of dextran present (6). Higher viscosities require additional time and energy consumption in the pans, crystallizers and centrifuges, and are responsible for lower sugar recoveries. In severe cases of dextran development - estimates are above 4000 ppm of dextran (6) - needle grain crystals (elongated along the C-axis) will frequently form, and make pan and centrifugal work very difficult. Dextran also has a melassigenic effect that decreases the yield of sugar. High levels of dextran in refinery molasses will cause problems in storage, transport and in marketing. The problems mentioned above can be anticipated by the systematic use of a good test for dextran levels in raw sugars, sweetwaters and early refinery streams. Although all polysaccharides have adverse effects on the processing of sugar cane, dextran is of primary importance in this respect particularly because the bacteria that make it are so common and dextran contamination is therefore so prevalent.

METHODS AND MATERIALS

Analyses

Several analytical methods have been developed to determine total polysaccharides found in sugarcane and its products. These analyses include polymers, such as starch and the indigenous sugarcane polysaccharide (ISP), that have developed from metabolic activities within the growing plant, and those, such as dextran, formed by microorganisms within the plant or during subsequent processing steps. A few of these analytical approaches are listed below, along with a method that is specific for dextran.

Types of Analyses. A complete structural and quantitative analysis of a dextran can be accomplished by exhaustive methylation of the compound, with subsequent hydrolysis and identification of the methylated saccharide units (13). This is a complex, difficult and lengthy procedure. Structural information may also be obtained by periodate oxidation of the dextran (10), which will show the frequency of various linkage types. This is also a lengthy procedure. There are various spectrophotometric analyses that depend on a colorimetric reaction (14), but the colorimetric reagents are not specific for dextrans and will react with other polysaccharides, and, unless the molecular weight of the dextran is known, results for concentration mean very little. This procedure is, again, rather complicated. Specific rotation (of over +200°) can be used to identify dextrans qualitatively.

There is a recently developed method that uses the dextranase enzyme

(15), with subsequent colorimetric analysis of the glucose produced. The enzyme attacks only the 1,6 linkages so that branch points are not accounted for. There appear to be little interference from starch or other polysaccharides but the procedure requires dialysis for over 2 days to remove sucrose.

For the purposes of routine analysis, the haze tests, involving precipitation of dextran from water solution by ethanol offer the best answer. The original simple haze analysis lacked specificity; all high molecular weight compounds precipitated. The version modified by Hidi, Keniry et al. (5) eliminates interference from starch and protein and provides some differentiation among molecular weight ranges, and so was used as the base test for development in this study.

In regard to the question of dextran tests in the sugar industry: it need not be necessary to have a test that shows structure, branching, molecular weight etc.; it is only necessary that the test use the same yardstick that measures dextran problems in sugar processing.

Haze Procedure. For this report, the modified dextran haze assay (5) was used. The modifications make the procedure more suitable for use in sugar mill laboratories. Both the original and the modified methods give values lower than the true dextran values as found by analysis of standard solutions (2,5).

Briefly, the modified procedure is as follows: A standard curve is prepared with a solution of Dextran 110 (110,000 mol wt) of known concentration. Aliquots containing 1 to 12 mg dextran are pipetted into 25 ml volumetric flasks, each containing 0.5 ml of 10% trichloroacetic acid (TCA) and 5.0 ml of 50% standard sucrose solution. Distilled water is added to make a total 12.5 ml before adding absolute ethanol, to the 25 ml mark, from a burette. Twenty minutes after mixing, the haze is read at 720 nm against water dilutions of duplicate aliquots. A straight line curve, absorbance vs dextran content, is obtained up to 10 mg of dextran, at which point the curve begins to flatten toward the dextran axis. In practice, the standard curve can be used only after the removal of destruction of sample components that affect the makeup of haze. In the case of mixed juice, excess ions are removed with ion-exchange resins before analysis. For process samples following juice heating, gelatinized starch is broken down with an enzyme prior to treatment with the mixed resins. Protein is precipitated with trichloroacetic acid.

In the dextran assay of raw cane juices, 60 ml of juice is shaken for 10 minutes with 2.0 g of a mixture of equal weights (dry basis) of Amberlite IR-120(H) and IR-45(OH)* resins. After separation of the resin by screening, a 50 ml aliquot of the juice is treated with 10 ml of 10% TCA, and the mixture is vacuum-filtered with 2% of a diatomaceous earth filter-aid. A 12.5 ml

*Use of a company and/or product name by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

aliquot of the filtrate is transferred into a 25 ml flask, ethanol is added, and the haze is read as described above.

For raw sugars, 50 ml of a 40° Brix solution of the sample is mixed with 0.05 g Kleistase GM-16 enzyme and the mixture is incubated at 55°C for 1 hour, with agitation every 15 minutes. The mixture is then shaken for 30 minutes with 10 g of the mixed resin before the resin is screened and rinsed with distilled water. The sample and washings are diluted to 100 ml, 10 ml of TCA are added, the mixture filtered, and the alcohol haze developed as above. For process materials, the procedure is the same as for raw sugar except that 10 g of the mixed resin is used. To avoid metal ion interference in low purity syrups, application of the procedure has been restricted to process materials having a true purity in excess of 80. Results below 20 ppm Bx are reported as 20 ppm.

The authors have made a few changes in the analytical procedures of Hidi, Keniry et al. (5). A calibration curve was prepared, as shown in Figure 3, with the commercial Dextran T2000 (2 million mol wt), and with a haze development time of 60 minutes. The higher molecular weight dextrans are believed to cause greater problems in processing (5), and the increased haze development time yields greater haze values and increases the accuracy of measurement. The effects of these two variables on haze development are shown in Figure 4. Another change in procedure was the substitution of the domestically available Mycolase(R), Code 4967-0 (GB Fermentation Industries Inc.) for the Kleistase GM-16 enzyme; there should, however, be no appreciable effect on the results. The last change was in the methods used for the removal of spent resins and in the filtration following the addition of TCA. Analytical grade filter aid was added to the digested sample containing enzyme residues and resins, and the mixture was filtered and washed, except in the case of mixed juice samples which were not washed, through a 47 mm Millipore fitted with prefilter only. The final filtration, after TCA treatment to precipitate proteins, was through the Millipore with 0.45 membrane and prefilter, but without the addition of filter aid. A sufficient quantity of turbidity-free filtrate can be obtained in the second filtration for testing.

Although the modified haze method for dextran analyses was not recommended for samples of true purity below 80, no trouble was experienced with such samples, and the analyses for low purity samples appear valid.

In order to expand the value of the dextran analyses in this work, total polysaccharides were also determined on all samples by the procedure of E. J. Roberts et al. (16).

PROCEDURE

Sampling. In Louisiana the worst operating conditions occur following a severe freeze that kills the cane plant, and splits the stalk, allowing the inner cell structure to be infected with bacteria. Cane in this condition will become sour during periods of warm and/or wet periods that are ideal for the formation of dextran. The juice sucrose, purity and pH values will drop as the organic acids content increases, until, in severe cases the remaining cane is abandoned. In an attempt to study dextran levels during several types of harvesting and processing conditions, samples of mixed

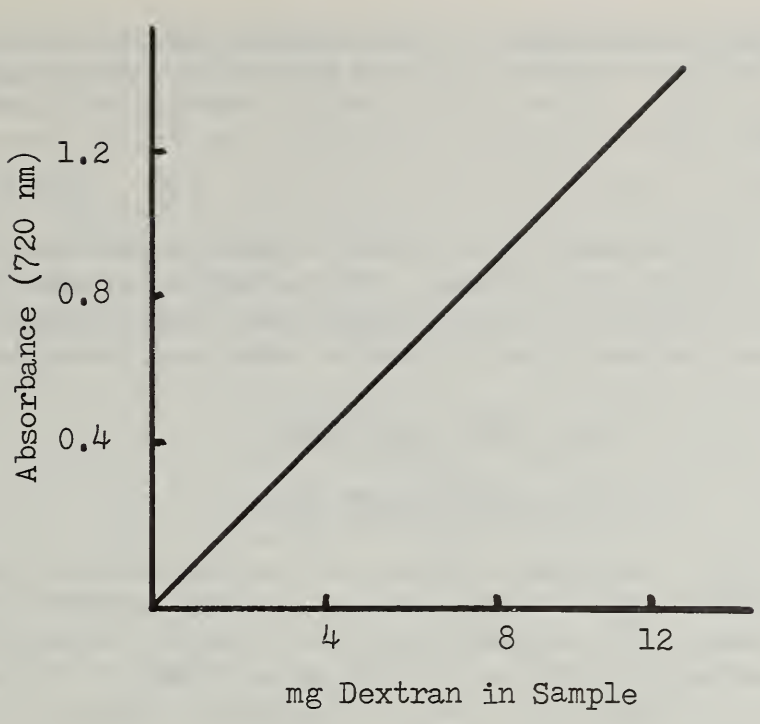

Figure 3. Dextran calibration curve with Dextran T2000, at 60 min development time.

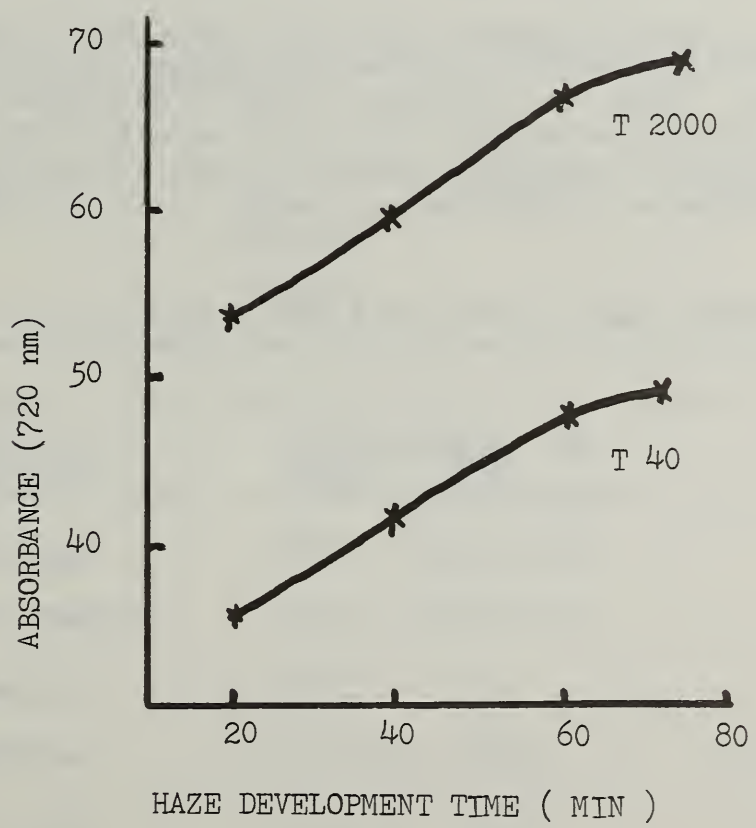

Figure 4. Effect of haze development time and dextran molecular weight on absorbance at 720 nm.

juice (mill juice), syrup, B-molasses, final molasses and raw sugar were collected, throughout the 1977 season, at two factories located centrally within the cane growing area. Mixed juice samples were frozen immediately for preservation. There were no samples obtained from frozen cane during this study.

Field Conditions. The harvest started under ideal conditions that deteriorated rapidly after the first few days. Wet conditions persisted generally until about December 10, although freeze damage never occurred in the 1977 crop. Field conditions corresponding to sample dates are shown in Table 1.

RESULTS AND DISCUSSION

Dextran Calibration Curve

Haze Development Time. A curve, Figure 4, was prepared to determine the effect of time on the absorbance values using a sucrose solution containing 6 mg of dextran per sample. For comparisons, the dextran values were obtained from the calibration curve, Figure 3. With Dextran T2000 (2 million mol wt), a haze development time of 60 minutes gave a 25% higher dextran value than the 20-minute time. With Dextran T40 (40,000 mol wt), the increase was 50%. This indicates that the 60-minute readings are preferable, especially when lower molecular weight dextrans are present.

Molecular Weight. The calibration curve for this study was set up on Dextran T2000 because of the special problems with higher molecular weight dextrans in processing. Since the absorbance value, from Figure 4, is a direct function of the molecular weight, the molecular weight distribution of dextran must be known for the materials under test before a correct calibration curve can be prepared. For example, samples containing Dextran T2000

Table 1: Relative field conditions during sampling periods (1977).

FACTORY	SAMPLE SERIES CODE	DATE	FIELD CONDITIONS
A	A-1	10/19	Dry
	A-2	10/25	Wet
	A-3	11/25	Prolonged wet
	A-4	12/17	Moderately wet
B	B-1	10/20	Dry
	B-2	10/24	Wet
	B-3	12/06	Prolonged wet

were analyzed and compared with those containing equal weights of Dextran T40. The T2000 values were 50% higher after 20 minutes and 30% higher than the T40 values after 60 minutes.

Factory Samples. The quality of cane entering a factory varies greatly, over short time intervals, as a result of cane maturity and variety, weather conditions, harvesting operations, degree of burn, delays in transport, cane storage conditions and trash content (leaves, weeds and soil). As a result, samples collected at one processing step are not always comparable with those from other steps in the process, except during prolonged periods of ideal harvesting conditions. Ideal conditions, at both factories, continued until after the first series of samples was collected. The minimum dextran contents, Table 2, were obtained at every processing step from these samples, and they probably represent the best that can be expected under good factory operations. At both factories there was a three fold increase in dextran during clarification and evaporation. This is probably the result of holding the hot limed juice in the clarifier (90 minutes) at below 100°C, at pH 7, and especially of the recirculation of the cooled clarifier-mud filtrate back to either the liming tank or the evaporators. There was also a greater buildup in dextran between the syrup and B-molasses samples than would be expected from just the removal of about 70% of the sugar solids. The dextran buildup between syrup and B-molasses was detected only at relatively low dextran levels. The highest

Table 2: Range of dextran and total polysaccharide values, ppm on Brix, in factory samples.

Sample	No. of Samples	Dextran Samples	Total Polysaccharides (X 1000)
Factory A:			
Mixed juice	4	80 - 790	12.2 - 45.7
Syrup	4	240 - 2100	4.1 - 10.8
B-molasses	4	960 - 3650	6.9 - 12.0
Final molasses	4	1070 - 4610	6.0 - 20.4
Factory B:			
Mixed juice	3	20 - 2910	27.4 - 30.8
Syrup	3	70 - 760	3.7 - 7.1
B-molasses	3	460 - 2330	9.1 - 14.9
Final molasses	3	620 - 1660	11.5 - 17.4
Raw sugar	3	20 - 500	0.7 - 2.6

dextran values were obtained from Factory B samples taken on the final day of operation. Samples of juice, syrup and molasses from this series were slightly sour, indicating sour cane from cleanup operations. This was the only case showing the removal of dextran during clarification.

Total polysaccharides, Table 2, were included in the study to determine possible relationships between them and the dextran levels. No direct relationship was observed. Mixed juice from well washed cane contained 25,000 to 30,000 ppm Brix of total polysaccharides; these are 80% - 85% removed during clarification. Appreciable quantities of soil in juice will interfere with the analyses of polysaccharides by settling out fractions of the starch before sampling, resulting in low values. Syrup analyses show that excess soil in juice also hinders the removal of polysaccharides during lime clarification. Syrups from high-soil juices contained twice the quantity of polysaccharides of those from clean juices.

Variations in soil content of juice are also probably responsible for the large variations in polysaccharide content of samples in these series. Apparently good cane washing operations are an essential step in the production of high quality raw sugar.

Raw Sugar Samples. Three commercial raw sugar samples were selected for comparison with the Louisiana raws from Factory B with respect to dextran and polysaccharide contents (Table 3). The Texas raw was darker in color, larger in grain size, and freer flowing than any of the three Factory B samples. The Philippine raw was very dark in color, very small in grain size, and was badly caked. The Brazilian plantation white was selected because of its history of being very difficult to crystallize. It was of mixed crystal size and shape, had been washed thoroughly, and in solution was very turbid and "dirty".

Table 3: Dextran and total polysaccharide values on selected sugar samples, ppm on Brix.

Sample	Dextran	Polysaccharides
Factory B raws	20 - 500	600 - 2600
Texas raw	90	1270
Philippine bulk raw	60	520
Brazil plantation white*	990	1570

*Difficulties encountered during crystallization; some needle grain formed; known to have dextran problem.

There is no relationship between the physical appearance of a raw sugar and its dextran or polysaccharide content. It appears that with proper affination, the Philippine raw would be a relatively high grade crystal, low in both dextran and polysaccharides. This particular Texas raw is similar to the Louisiana raw that was produced under favorable harvesting conditions. The authors will not speculate on the dextran and total polysaccharides contents of the Brazilian sugar prior to intensive washing, but it appears that a higher percentage of the dextran was retained by the crystal.

CONCLUSIONS

The degree of dextran formation in the raw sugar industry is quite variable, as demonstrated by analyzing samples from two factories in Louisiana. A total of seven series of samples, consisting of mixed juice, syrup, B-molasses, final molasses and raw sugar (3 series only), were analyzed for dextran and total polysaccharides. Low dextran values were obtained on two series processed during ideal harvesting conditions, but the dextran values increased dramatically as the harvesting conditions deteriorated. Dextran formation continued throughout the juice clarification and sugar boiling steps, with one exception: samples taken on the last day of operation at one factory were slightly sour, high in dextran, with the mixed juice dextran showing 74% removal during clarification and concentration. The dextran from sour cane was probably of high molecular weight that was readily removed by clarification.

Total polysaccharides in mixed juice were in the range of 30,000 ppm Brix, with 80% removal during clarification in samples relatively free of soil. Appreciable quantities of soil in juice adversely affected polysaccharide removal during clarification, as well as the analytical determinations. Polysaccharide data were very erratic throughout the series, and they had no direct relationship with the dextran data.

The dextran and total polysaccharides that were determined on samples of Brazil plantation white sugar were included in the data to give observed maximum/minimum ratios of 50 for dextran, and 5 for polysaccharides. With such large variations in dextran load entering a refinery, it seems appropriate for each refinery to establish a routine dextran check program at several key processing steps. Expected deviations in dextran levels expected, based on raw sugar analysis, would alert operating personnel to housekeeping or other problems relating to dextran within the refinery.

Dextran formation can be a dangerous source of sucrose loss in a refinery, as well as a problem in pan work and especially in low grade recovery.

This study points out problem areas in dextran contamination. The modified haze test used here appears to be the best solution at present, with regard to speed and specificity, to the search for a suitable dextran test for sugar processing.

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DISCUSSION

J. F. Dowling (Refined Syrups): You can judge a raw sugar for dextran content by looking at the ratio of axes of the sugar crystals. Tate and Lyle have developed this method. 1/

If a raw sugar comes in at 600 ppm dextran, the chances are that the refined sugar you make from it will be 500 ppm. The dextran will build up in the remelt system and will lead to sugar loss to molasses because the sugar crystals will be elongated, and harder to purge and wash.

Dextran in the refined sugar also causes some problems in the candy industry with deformation of extruded shapes.

The haze test is not very specific. The amount of haze depends upon molecular weight, and there is interference from everything that will precipitate in 50% alcohol, but it is still the best available rapid dextran test. We need a better rapid dextran test, and we need to know better how to reduce dextran in refining. One of the causes of the dextran increase in the last 10 years is probably mechanical harvesting. There are certain origins, especially Brazil, where dextran is constantly higher. Philippine sugar is consistently low in dextran.

E. E. Coll: I understand that in Jamaica they have terrible infections of the dextran-producing organism in all the fields. That is the reason why the cane that gets damaged there has so much dextran. I don't know about the Philippines. Perhaps they have a quick operation, good washing, and good sanitation, all conducive to low dextran content.

J. F. Dowling: Dextran can be produced in the refinery, especially in dust collectors. Also if you run a remelt house at low brix, dextran will be

1/ Imrie, F. K. E., and Tilbury, R. H. Polysaccharides in sugar cane and its products. Sugar Technol. Reviews. 1, 291-361, (1972).

generated over weekends and shutdowns. In the refinery, brix control and sanitation are the key. We can do something about dextran production on our own premises, but if it is already in the raw sugar, we are stuck with it. We don't have a specific refining process to remove dextran. It mostly goes into the refined sugar.

E. E. Coll: I think that if a sugar refinery was built and operated for high thermal efficiency, the dextran problem would be gone. Everything would be compact and sweetwaters with their possibility of spoilage and dextran formation would be minimized.

M. A. Clarke (CSRRP): I would like to clarify one point. That Brazilian plantation white sugar referred to in Table 3 is not typical of Brazilian sugar, nor of plantation white sugar. This particular sample was sent to us because it had bad needle grain and we had requested samples like that. We had a look at it just to see how much dextran it contained, and compared it with a sugar that had no needle grain. One of our goals in this study is to see how much dextran must be present before needle grain is observed. One further point on Brazilian sugar: the cane harvest in Northern Brazil this year took place under unusual condition of heavy rains. There was much more field soil and damaged cane than usual and so the raw sugar produced there this year was higher in dextran than usual. This was not the case in Southern Brazil-only in the North.

E. E. Coll: I would like to make an additional point. I have been analyzing some freshly cut canes directly from variety outfield tests. One variety had 300 to 600 ppm dextran in the juice. That was a variety which was on the way out because it has a history of stalk splitting. These samples were taken near the end of the season and apparently these canes had split and I picked up the dextran. With one other variety I got merely a trace of dextran. All the other commercial varieties didn't even have a trace. So, dextran is not in healthy cane, it is in damaged cane. There has to be a lot of work done in the harvesting and storage and management of cane.

NON-SUCROSE CHANGES DURING SUGAR PROCESSING

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ABSTRACT

An accurate and precise gas liquid chromatographic procedure using oximation and silylation has been developed for the three major sugars in cane sugar factory products. The method was applied to samples of evaporator syrup and final molasses from two Huletts factories over a nine-month crushing season. Conventional factory control analyses as well as determination of chloride, amino-nitrogen and non-fermentable reducing substances were also carried out on these samples. Using chloride as a base it has been shown that reducing substances other than fructose or glucose are formed during boiling house operations and that increased fructose/glucose ratios are due mainly to a loss of glucose. There was no apparent seasonal trend in amino nitrogen levels but a significant decrease was found between syrup and molasses. The influence of the major optically-active impurities on the pol measurement is discussed and a correlation established between pol and the three sugars - sucrose, glucose and fructose. There is a slight increase in optically-active substances between syrup and molasses. Part of this increase is apparent and due to the effect of dry lead acetate on the pol analysis.

INTRODUCTION

Non-sucrose impurities entering the factory in the cane are largely beyond the mill's control. Glucose and fructose will comprise a large proportion of this non-sucrose. Irvine (1) has demonstrated a varietal and seasonal difference in the fructose/glucose (F/G) ratios for Lousiana cane juice (0,51 - 0,83) - with early maturing varieties showing higher F/G ratios than later maturing varieties. We have generally found South African juices to have F/G ratios slightly greater than unity (2, 3, 4). However, non-sucrose may also be formed during processing so that changes can occur in both the absolute and relative levels of these impurities.

During processing some sucrose is undoubtedly hydrolysed to glucose and fructose, the extent of the reaction depending on pH, temperature and the ionic environment (5). Radioactive tracer studies have indicated the partial decomposition of sucrose during molasses formation (6). Alkalinity and temperature changes occurring in the factory will also cause decomposition, fragmentation, condensation and isomerisation reactions between the monosaccharides (mainly glucose and fructose) and other im-

purities. Most of the mannose in molasses originates from the isomerisation of fructose (7).

Although fructose is considered to be more sensitive to low pH/high temperature conditions than glucose, and invert solutions prepared by acid hydrolysis give F/G ratios less than unity (8) there is ample evidence that both cane and beet final molasses generally contain a higher proportion of fructose than glucose (2, 9, 10, 11). However, ratios less than one have been reported by Carruthers (12) for beet molasses and by Gardiner (13) and Mauch (14) for cane molasses. Dowling (15) has reported ratios less than unity for refinery blackstrap molasses.

Modern instrumental techniques are being used more frequently to estimate individual constituents more specifically, more accurately and more precisely. Gas chromatography (g.c.) provides a useful tool for the specific determination of the individual sugars in factory products. An accurate procedure for measuring sucrose by g.c. in mixed juice and molasses has been developed in this laboratory (16) and applied routinely (17). Although this same silylation technique can be used to measure glucose and fructose, several assumptions regarding mutarotation equilibria are involved and quantitative evaluation is often difficult because the monosaccharides produce a large number of overlapping anomeric peaks. Consequently it is preferable to block the aldehyde or keto groups before silylation. Methyloxime or oxime derivatives are frequently used to give simpler chromatograms with increased sensitivity. We used Brobst's (18) oximation - silylation procedure, but found that sucrose hydrolysis occurred during oximation. This side-reaction was eliminated by increasing the pH of the oximation reagent. (19)

In an attempt to acquire some insight into the fate of certain non-sucrose constituents in the boiling house this modified g.c. procedure was applied routinely throughout the season to measure sucrose, glucose and fructose in evaporator syrup and final molasses from Empangeni and Mount Edgecombe Mills.

To enable direct comparison of the input (syrup) and output (molasses) streams chloride was monitored. Since chloride is highly soluble and unlikely to undergo chemical reaction, it is an ideal reference.

An automated colorimetric procedure was used to measure amino-nitrogen in both syrup and molasses since amino compounds have been implicated in glucose losses.

The chemical control of a sugar factory is usually based on direct polarisation (pol) as an estimate of sucrose for simplicity and convenience. However, there is usually no direct relationship between pol and sucrose, particularly with low purity products. Any optically-active impurity (e.g. monosaccharides, oligosaccharides, gums, starch, organic or amino acids) will influence pol. The presence of inorganic salts can also modify the optical activity of some components and lead to analytical errors (20).

Fructose and glucose are usually the most abundant optically-active impurities in cane products and hence make the largest contribution to the 'pol error'. Further, any changes in the relative amounts of fructose and glucose during processing or storage can seriously affect pol based factory data. (21)

EXPERIMENTAL

The syrup and final molasses samples analysed were weekly composite samples from each factory during the 1977/78 season. Syrup samples were preserved with mercuric chloride solution (22) (about five drops per litre). All samples were refrigerated (-10°C) prior to analysis.

The methods of analysis were as follows :

1) Refractometer brix :

Syrup samples were diluted 1 in 3 with distilled water and molasses 1 in 5. The brix of the filtered solutions was determined with a precision refractometer. Details appear in the Laboratory Manual for South African Sugar Factories (22).

2) Pol :

Diluted solutions of syrup or molasses were clarified using dry lead - subacetate (1 g / 100 ml of 1 in 3 syrup dilution or 5 g / 100 ml of 1 in 10 molasses dilution). The clarified filtrate was used to determine the pol. (22)

3) Reducing substances : were determined by the Lane and Eynon titration using the S.R.I. method. (23)

4) Non-fermentable reducing substances :

The Java Sugar Experiment Station procedure was used for fermentation. (24) Reducing sugars on the filtrate were determined using the Luff Schoorl method. (22)

5) Sucrose :

a) Sucrose was determined on molasses using the Lane and Eynon titration after acid hydrolysis according to the Mackay method. (23)

b) Sucrose on syrup and molasses samples was determined gas chromatographically as the TMS ethers using the silylation technique of Brobst and Lott. (25) Details are included in Appendix 1.

6) Glucose and Fructose :

The monosaccharides were oximated and the resulting oximes silylated prior to g.c. analysis using a modification of the method of Brobst. (18) Details are included in Appendix 1.

7) Chloride :

This was determined by potentiometric titration as described by Comrie. (26) Aliquots contained 5 g syrup or 1 g molasses.

8) Amino Nitrogen :

An automated adaptation of the colorimetric method described by Carruthers (27) and based on that of Eveleigh (28) was used. Details appear in Appendix 2.

RESULTS AND DISCUSSION

A : Precision and Accuracy of the Method

All samples were massed in duplicate. The precision of the sucrose analysis was 0,6% relative for the entire season (i.e. $\pm$ 0,2 units for a molasses containing 30% sucrose). The analytical scatter was halved (C.V. 0,3 - 0,4%) after converting to more efficient capillary columns. This compares favourably with the sucrose precision obtained for the direct silylation-isothermal g.c. separation (i.e. C.V. better than 0,5% (16)). Fructose or glucose precision was of the order of 2%, but was considered adequate (i.e. $\pm$ 0,2 units for concentrations of 10% or about $\pm$ 0,03 units at the 1,5% level).

The repeatability of the method was further checked by re-analysing syrup or molasses samples up to 10 weeks after storage at -10°C. Fructose and sucrose analyses were not significantly different at the 95% confidence level, nor were the glucose analyses on syrup. However, the analyses of molasses for glucose showed a consistent and significant decrease of almost 3% relative (initial mean for 28 samples : 6,04% glucose compared with 5,87% ten weeks later). We felt this difference was acceptable in practice since analyses are normally carried out shortly after the receipt of samples and not 2 - 3 months later.

TABLE 1 - Analytical Precision

Product	Samples	Treatment	Test	Sugar		
				Fructose	Glucose	Sucrose
Syrup	180	duplicates *	C.V.(%)	1,9	2,3	0,6
	111	duplicates **	C.V.(%)	-	-	0,3
	22	stored (-10°C)	C.V.(%)	2,4	3,2	0,6
			t	0,084	1,037	0,552
Molasses	136	duplicates *	C.V.(%)	1,2	1,5	0,6
	118	duplicates **	C.V.(%)	-	-	0,4
	28	stored (-10°C)	C.V.(%)	3,6	4,0	0,8
			t	1,007	3,180	0,537

* using packed and capillary columns

** using capillary columns

The accuracy of the analysis was established in three ways :

1) The sucrose results were compared with those obtained using direct silylation and isothermal g.c. conditions which has been shown to be precise and accurate.(16) 30 samples of syrup and molasses showed no significant difference when analysed by the two methods (t = 0,071, pooled C.V. $\pm$ 0,7%). Hence the modified oximation procedure does not affect the accuracy or precision of the sucrose analysis. In our experience the method of Brobst (18) consistently overestimated sucrose by about 2% relative.

2) Mixtures of the three sugars were prepared at approximately the levels found in factory products. These solutions were analysed for fructose, glucose and sucrose at the same time as routine samples and the results used to estimate the polarisation (details in Appendix 3). The measured pol agreed well with the calculated pol, substantiating the accuracy of the g.c. procedure. (Table 2)

TABLE 2 - Accuracy Test - Synthetic Samples

Gas Chromatographic analysis					
Fructose	Glucose	Sucrose	Pol_d	Pol	Pol/Pol_d
6,2	4,0	30,3	25,1	25,3	1,008
10,2	7,7	30,3	22,5	23,0	1,022
6,0	3,5	26,2	20,9	20,4	0,976
6,0	5,3	27,6	23,7	24,4	1,030
5,0	4,6	27,2	24,4	24,0	0,984
5,6	4,4	26,5	22,5	22,1	0,982
7,0	5,1	28,5	23,1	22,9	0,991
4,9	8,0	28,5	28,3	28,5	1,007

This technique has since been incorporated as a check procedure for the reliability of routine g.c. analyses.

3) Varying amounts of fructose, glucose and sucrose were added to samples of the same molasses. As the amount of sugar added increased, smaller weights of molasses were taken so that the final concentration of sugars was similar in all samples. Since the accuracy with which 10 - 50 mg of fructose or glucose can be weighed directly is questionable these sugars were added as aliquots of 1% solutions or else the sample was scaled up ten times. The results of 15 recovery runs for the three sugars are included in Table 3. The procedure was quantitative - 100,6; 100,6; 98,1 per cent recovery for sucrose, glucose and fructose respectively. However, the precision achieved (2,9%; 6,3%; 8,1% for the three sugars) was disappointing when viewed against the sample precision of 0,5%; 1,9% and 1,5% maintained throughout the season on over 700 sample duplicates. Our only explanation for this high scatter is that the variance of the recovery procedure will be higher than that normally achieved since a further analytical step is involved :

$$\text{Variance}_{\text{Recovery}} = \text{Variance}_{\text{calibration}} + \text{Variance}_{\text{sample}} + \text{Variance}_{\text{spiked sample}}$$

TABLE 3 - Recoveries of sucrose, glucose and fructose added to molasses samples - accuracy test

Sugar	Approx. Mol (g)	Added (mg)	Re-covered (mg)	Re-covered (%)	Approx. Mol (g)	Added (mg)	Re-covered (mg)	Re-covered (%)	Approx. Mol (g)	Added (mg)	Re-covered (mg)	Re-covered (%)
Sucrose	1,8	52,7	53,3	101,1	1,9	57,1	56,7	99,3	1,9	51,6	49,6	96,1
	1,6	100,6	106,6	106,0	1,6	101,2	105,3	104,1	1,8	100,7	96,3	95,6
	1,4	149,8	152,5	101,8	1,4	150,8	154,5	102,5	1,6	154,6	149,8	96,9
	1,2	201,3	205,3	102,0	1,3	200,8	205,8	102,5	1,4	200,0	202,4	101,2
	1,0	249,8	253,0	101,3	1,1	249,5	251,1	100,6	1,2	250,0	245,7	98,3
												100,6
												± 2,9
Glucose	1,9	8,8	9,6	109,1	1,8	8,8	10,3	117,1	18,5	92,4	92,1	99,7
	1,7	17,6	16,3	92,6	1,7	17,6	16,9	96,0	17,0	179,6	166,5	92,7
	1,5	26,4	26,2	99,2	1,6	26,4	26,0	98,5	15,5	265,0	272,3	102,8
	1,5	35,2	36,1	102,6	1,4	35,2	35,1	99,7	14,0	352,7	350,1	99,3
	1,3	44,0	45,1	102,5	1,3	44,0	45,4	103,2	12,6	445,9	421,6	94,6
												100,6
												± 6,3
Fructose	1,9	8,8	9,7	110,2	1,9	8,8	8,9	101,1	18,5	100,3	94,8	94,5
	1,8	17,6	16,4	93,2	1,7	17,6	-	-	17,0	210,8	181,6	86,2
	1,6	26,4	26,8	101,5	1,6	26,4	28,4	107,6	15,5	300,4	289,7	96,4
	1,6	35,2	35,4	100,6	1,4	35,2	31,1	88,4	14,0	399,8	355,6	88,9
	1,2	44,0	46,7	106,1	1,2	44,0	47,7	108,4	12,6	501,4	455,3	90,8
												98,1
												± 8,1

B : Non-Sucrose Changes

The non-sucrose levels in syrup and molasses have been expressed relative to the chloride content. The inherent accuracy and precision of the chloride analysis is well-known and no difficulties were encountered in maintaining a relative error of less than 0,3% for duplicate determinations. Any chloride added to syrup as preservative was less than 0,25% (i.e. within the analytical scatter) and so was disregarded. Although it is possible to achieve better precision than this, we felt it unnecessary when viewed against the magnitude of the changes measured. Chloride monitoring lends itself well to areas of process where the main change is removal of sucrose and the subsequent concentration and inter-reactions of organic impurities.

The seasonal levels of non-sucrose components in syrup and molasses at Empangeni and Mount Edgecombe are summarised in Table 4.

TABLE 4 - Non-Sucrose in Syrup and Final Molasses (Non-Sucrose expressed per g chloride)

Mill	Product	Analysis		April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.
EM	Syrup	R.S.	(g)			7,16	6,27	6,12	5,91	5,98	6,02	7,17	7,49
		F+G	(g)			6,98	5,97	5,84	5,58	5,89	5,56	6,47	6,90
		F	(mM)			19,2	16,8	16,4	15,7	16,2	15,0	17,2	19,0
		G	(mM)			19,6	16,4	16,0	15,3	16,5	15,8	18,7	19,6
		Am-N	(mM)			7,0	6,7	7,5	8,2	8,2	6,9	7,2	7,4
	Molasses	R.S.	(g)			8,80	7,39	6,92	6,77	6,37	6,73	7,26	8,24
		F+G	(g)			7,66	5,87	5,58	4,93	4,93	5,14	5,63	6,42
		F	(mM)			22,9	17,3	17,4	16,2	16,3	16,3	17,6	19,9
		G	(mM)			19,7	15,3	13,7	11,2	11,1	12,3	13,9	15,8
		Am-N	(mM)			4,5	4,5	5,2	5,6	5,6	5,2	4,3	4,6
ME	Syrup	R.S.	(g)	11,13	11,61	10,74	9,47	8,85	6,80	6,11	6,45	7,90	8,43
		F+G	(g)	10,98	11,70	10,97	8,95	8,89	6,82	5,98	5,84	7,00	7,70
		F	(mM)	29,9	31,8	30,2	25,9	25,4	19,8	17,3	16,7	19,6	21,9
		G	(mM)	31,1	33,2	30,7	23,8	24,0	18,1	16,0	15,7	19,3	20,9
		Am-N	(mM)	9,3	9,9	10,3	10,6	10,7	9,6	9,9	9,8	10,9	10,9
	Molasses	R.S.	(g)	12,43	13,45	12,93	10,84	10,55	8,32	6,76	7,24	8,43	9,68
		F+G	(g)	10,73	11,49	11,20	9,11	8,45	6,35	5,05	5,43	6,32	7,89
		F	(mM)	32,0	35,1	34,4	29,4	27,8	21,6	17,4	18,5	21,2	24,9
		G	(mM)	27,6	28,7	27,8	21,2	19,2	13,6	10,6	11,7	13,9	18,9
		Am-N	(mM)	6,1	6,7	7,6	8,0	8,1	7,3	6,8	6,9	7,4	7,6

Key: R.S. reducing substance
F fructose
G glucose
Am-N amino-nitrogen
mM milli-moles

The F/G ratios for the two streams at each mill are presented in Table 5.

TABLE 5 - F/G Ratio for Syrup and Final Molasses at EM and ME

	EM		ME	
	Syrup	Molasses	Syrup	Molasses
April			0,96	1,16
May			0,96	1,22
June	0,98	1,16	0,98	1,24
July	1,02	1,13	1,09	1,39
August	1,03	1,27	1,06	1,45
Sept.	1,03	1,44	1,10	1,59
Oct.	0,98	1,47	1,08	1,64
Nov.	0,95	1,33	1,06	1,59
Dec.	0,92	1,27	1,01	1,53
Jan.	0,97	1,25	1,05	1,32
Min.	0,92	1,13	0,96	1,16
Max.	1,03	1,47	1,10	1,64

It can be seen that the F/G ratio always increased between syrup and molasses and that this ratio peaked during October at both mills. The F/G ratio in syrup, although close to unity, also showed a definite seasonal trend. Ratios in both syrup and molasses were consistently higher at Mount Edgecombe than at Empangeni. This distinct change in the relative amounts of fructose and glucose both seasonally and during boiling is illustrated in Fig. 1.

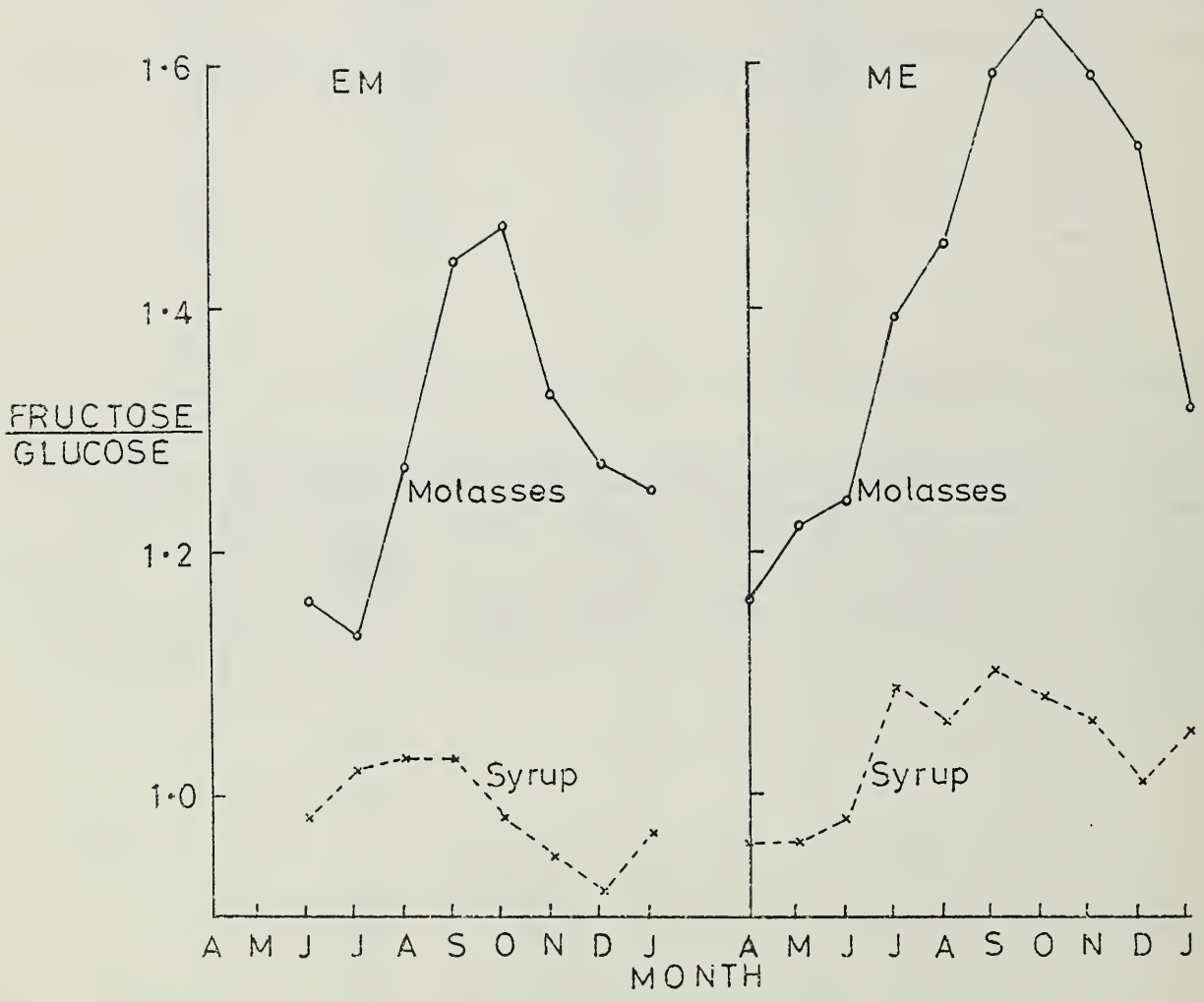

FIGURE 1 - Seasonal Variation in F/G ratio for Syrup and Molasses

In addition to the main study reported here, fructose and glucose were also determined on a few samples of cane molasses from other mills in South Africa and other countries. These all showed F/G ratios greater than unity, indicating that the effect is certainly not localised. (Table 6)

TABLE 6 -

Source	Fructose	Glucose	Sucrose	F/G
Australia	4,7	3,6	34,5	1,31
Brazil	8,3	7,9	38,2	1,05
Mozambique	7,5	4,5	35,0	1,67
East Africa/ Brazil	8,6	6,6	32,6	1,30
South Africa -				
Mill A	6,1	4,9	28,4	1,24
Mill A	8,5	6,9	28,6	1,23
Mill B	9,1	5,5	26,3	1,65
Mill B	7,7	3,2	27,9	2,41

Fructose and glucose were also determined on liquors from Huletts central refinery. This refinery processes raw sugar from a number of South African mills, and in the 1977/78 season raws from EM, ME and Mill A comprised 40% of the refinery's total melt. In contrast to the results for the mills, refinery liquors always showed less fructose than glucose, generally of the order 0,7 - 0,8.

TABLE 7 -

Process Stream		Fructose	Glucose	Sucrose	F/G
Saturator supply	(July)	< 0,05	< 0,05	67,7	-
Brown liquor	(June)	0,14	0,19	64,5	0,7
	(July)	< 0,05	< 0,05	66,1	-
Fine liquor	(June)	0,14	0,18	64,3	0,8
	(July)	< 0,05	< 0,05	65,6	-
Jet off char		0,32	0,41	59,4	0,8
Return syrup	(July)	0,65	0,95	67,3	0,7
Exhaust molasses	(Aug. 1977)	4,2	5,2	36,6	0,8
	(June 1978)	6,1	8,2	37,5	0,7
	(July 1978)	5,7	8,1	37,7	0,7
Rotoclone sweetwater	(Aug. 1977)	0,27	0,34	7,1	0,8

At both EM and ME the proportion of reducing substances (R.S.) other than fructose and glucose increased throughout the season, in syrup, with the ratio (F+G)/R.S. dropping below 0,94 after October. Molasses showed a similar seasonal trend, but the proportion of other reducing substances increased significantly between syrup and molasses, with up to 27% of the reducing substances being neither fructose nor glucose. (Fig. 2)

Although total fructose and glucose decreased during boiling, the amount of reducing substances increased. During the latter part of the season non-fermentable reducing substances were measured in molasses. A good correlation between non-fermentable reducing substances (NFRS) and reducing substances other than fructose and glucose (R.S. - F - G) was found :

$$(RS - F - G) = 0,35 + 1,02\ NFRS$$

$$(r = 0,81 \text{ for } 12 \text{ pairs})$$

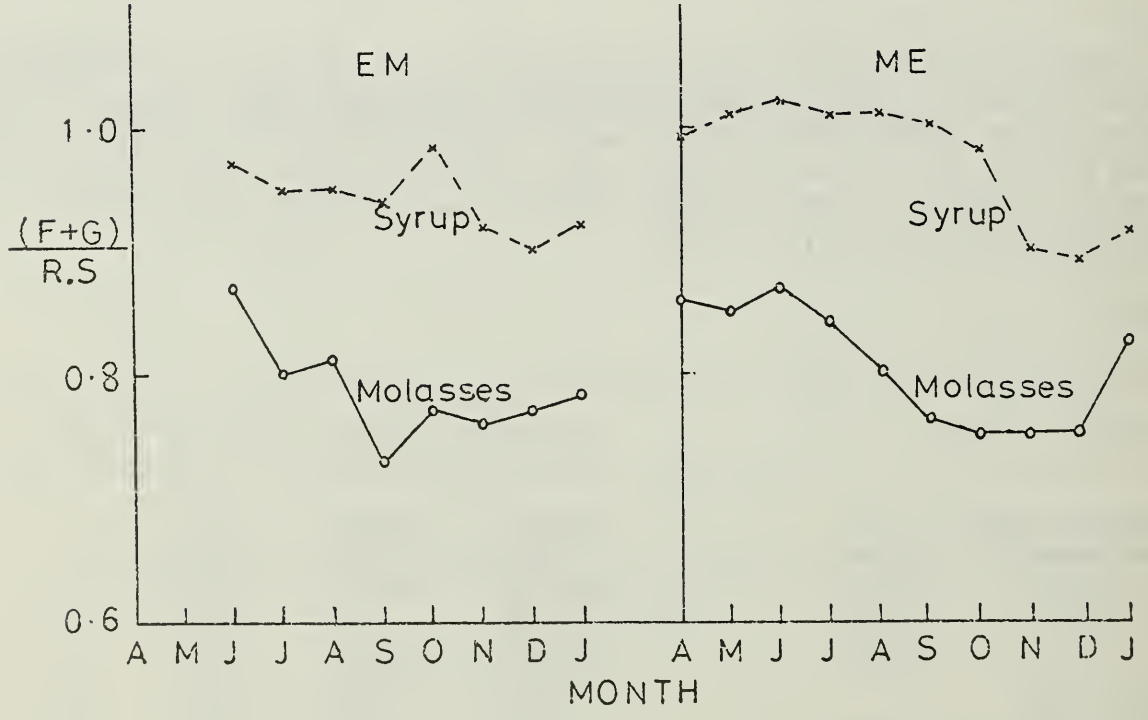

FIGURE 2 - Proportion of Reducing Substance due to Fructose and Glucose

In general, there was an increase in fructose between syrup and molasses. This could be indicative of sucrose inversion or of glucose/fructose interchange. The increase averaged 6% at Empangeni and 10% at Mount Edgecombe.

By contrast there were large decreases in the glucose levels between syrup and molasses. The average loss for the two mills was 19%, with the largest drop (33%) occurring in October. (Fig. 3)

Two molasses samples were stored at ambient temperatures (6 - 9 months) and subsequently re-analysed (Table 8). Glucose losses were considerable, with some fructose loss and little sucrose destruction. It is evident that the composition of final molasses can change extensively during storage.

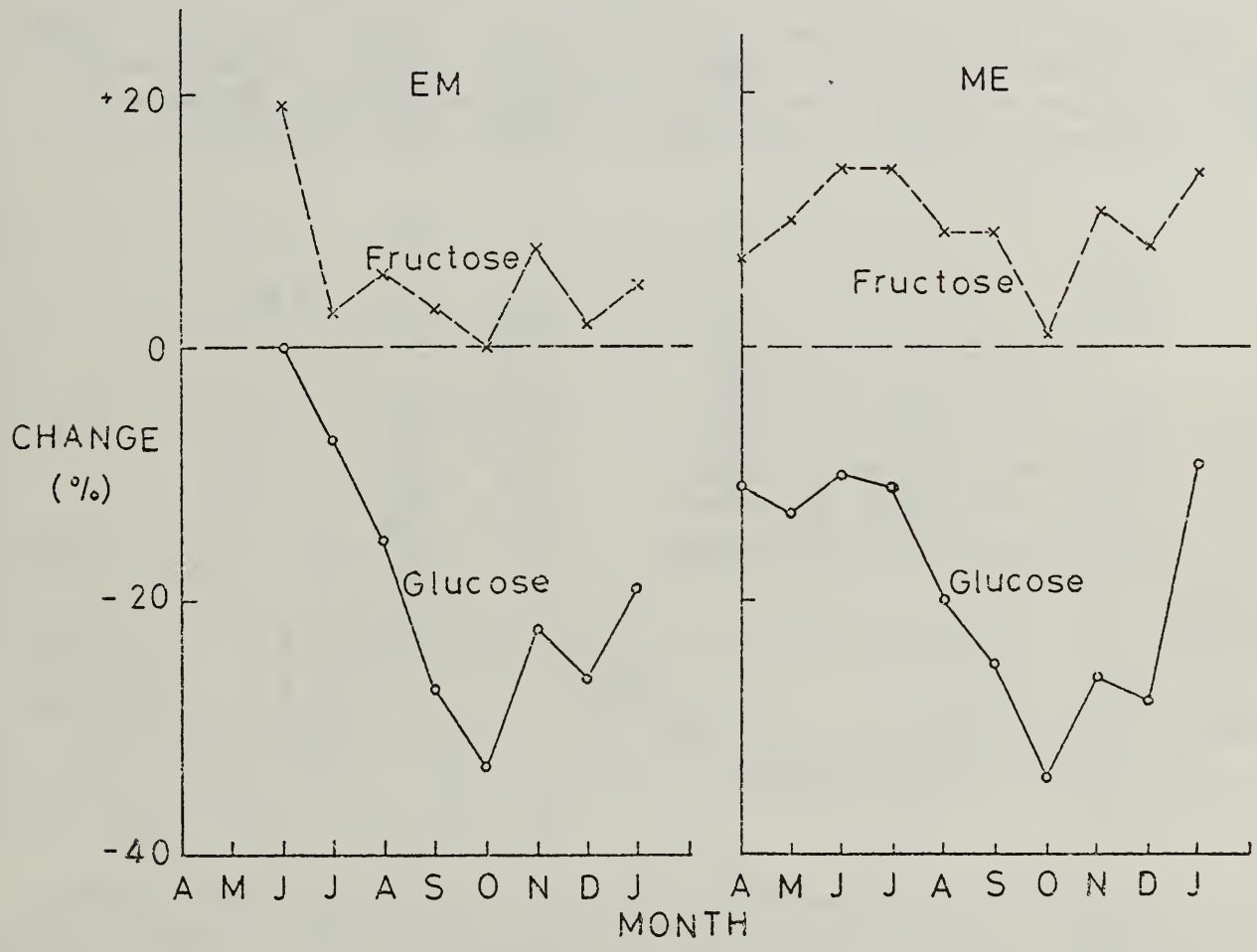

FIGURE 3 - % Change in Fructose and Glucose between Syrup and Molasses

TABLE 8 -

	Fructose		Glucose		Sucrose		Reducing Substances	
	Original	Repeat	Original	Repeat	Original	Repeat	Original	Repeat
Sample 1	9,6	9,1	5,5	4,3	26,1	26,0	19,7	18,3
Sample 2	7,7	7,4	3,2	2,6	27,9	27,6	15,1	14,2

There was no obvious trend in amino-nitrogen levels in syrup, although levels at EM seemed to peak September - October. However, approximately one third of the amino-nitrogen was destroyed between syrup and molasses. Levels at ME were generally higher than at EM for both syrup and molasses.

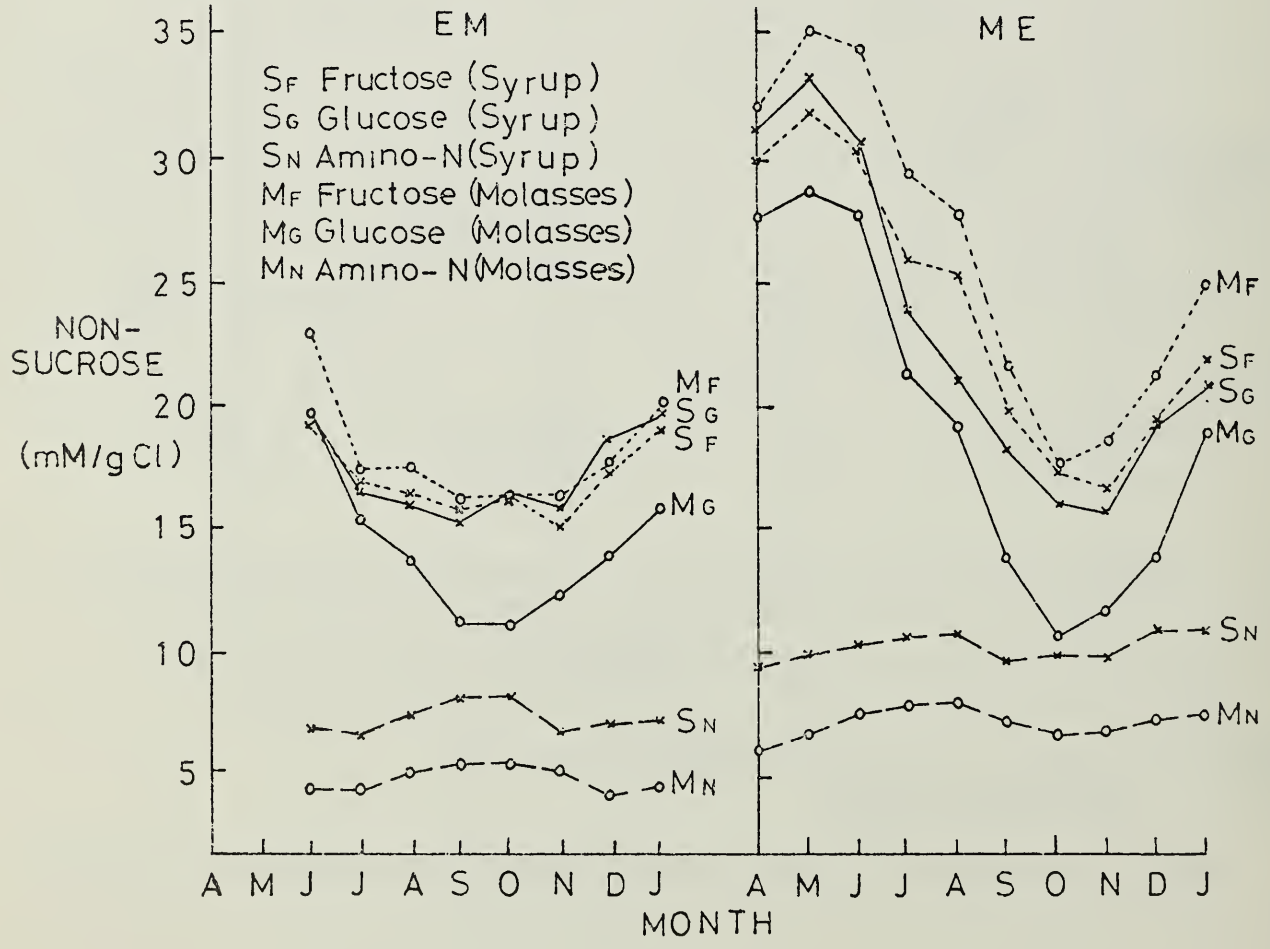

FIGURE 4 - Seasonal Comparison of Non-Sucrose in Syrup and Molasses

Three sets of samples (syrup; A-molasses; B-molasses and C-molasses) were monitored over a three week period to establish whether non-sucrose changes were more prevalent at any one particular stage of boiling. (Table 9)

Pol became increasingly inaccurate as a measure of sucrose whilst the ratio (F+G)/RS decreased. There was an increase of both fructose and glucose between syrup and A-molasses. From A-molasses to final molasses glucose was destroyed more rapidly than fructose so that the F/G ratio showed an overall increase between syrup and final molasses.

TABLE 9 - Effect of successive boilings on Non-Sucrose

	Pol/S	P/P_d	F/G	(F+G)/R.S.	F/Cl^-	G/Cl^-
1 - Syr	1,00	1,01	0,94	0,95	3,7	3,9
A	0,98	1,03	1,08	0,86	4,2	3,8
B	0,98	1,11	1,22	0,82	4,0	3,3
C	0,92	1,21	1,54	0,74	4,0	2,6
2 - Syr	0,99	1,01	1,06	0,92	4,5	4,2
A	0,98	1,04	1,17	0,87	5,3	4,5
B	0,97	1,10	1,19	0,82	4,8	4,0
C	0,93	1,22	1,24	0,84	4,5	3,6
3 - Syr	1,00	1,01	1,04	0,91	3,4	3,3
A	1,00	1,04	1,10	0,84	3,9	3,5
B	0,99	1,09	1,21	0,82	4,0	3,3
C	0,95	1,18	1,35	0,82	4,3	3,2

C : Sucrose Estimation in Factory Products

Although quantitative g.l.c. methods for carbohydrate estimation can be specific, reproducible and accurate and can be reliably applied on a routine basis, the day-to-day maintenance of high precision and accuracy is not always easy. (17, 29, 30)

Besides this aspect g.l.c. instrumentation involves considerable capital outlay, so that easier, rapid methods of measuring 'apparent' sucrose will continue to be used in routine factory control. Such techniques include chemical methods such as the Lane and Eynon titration and physical methods such as direct polarisation. Both methods are widely used for factory control purposes.

The relationship between the different methods will be discussed with reference to the pol, sucrose, fructose and glucose data for syrups from EM and ME and molasses from EM, ME and Mill B for the 1977/78 season as presented in Table 10.

TABLE 10- Syrup and Final Molasses Analysis

Mill	Product	Analysis	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.
EM	Syrup	Pol	–	–	54,7	55,9	56,9	56,8	57,3	57,9	54,3	52,2
		S_{gc}	–	–	55,6	56,3	57,2	56,6	57,3	57,7	54,7	52,4
		F	–	–	1,34	1,23	1,25	1,20	1,22	1,17	1,37	1,54
		G	–	–	1,37	1,20	1,22	1,17	1,24	1,23	1,49	1,59
		Pol_d	–	–	54,9	55,6	56,5	55,9	56,7	57,1	54,0	51,7
		Pol/S_{gc}	–	–	0,98	0,99	1,00	1,00	1,00	1,00	0,99	1,00
		Pol/Pol_d ...	–	–	1,00	1,00	1,01	1,02	1,01	1,01	1,01	1,01
		F/G	–	–	0,98	1,03	1,02	1,03	0,98	0,95	0,92	0,97
	Molasses	Pol	–	30,3	28,4	29,1	30,5	29,8	30,7	30,6	31,1	30,4
		S_{LE}	–	32,7	31,3	31,4	32,9	32,3	32,8	32,6	33,9	33,0
		S_{gc}	–	31,4	29,8	30,7	31,7	31,2	31,0	30,9	31,9	31,3
		F	–	8,5	8,6	6,8	7,0	6,5	6,3	6,1	6,6	6,9
		G	–	7,8	7,4	6,0	5,5	4,5	4,3	4,6	5,2	5,5
		Pol_d	–	26,1	24,0	26,3	26,6	26,0	25,9	26,3	27,1	26,3
		Pol/S_{gc}	–	0,97	0,95	0,95	0,96	0,96	0,99	0,99	0,97	0,97
		Pol/Pol_d ...	–	1,17	1,18	1,11	1,15	1,15	1,19	1,16	1,15	1,16
		S_{LE}/S_{gc} ...	–	1,04	1,05	1,02	1,04	1,04	1,06	1,06	1,06	1,05
		F/G	–	1,09	1,16	1,13	1,27	1,44	1,47	1,33	1,27	1,25
ME	Syrup	Pol	54,3	55,6	57,3	58,4	57,7	58,6	58,7	58,1	57,3	55,9
		S_{gc}	54,6	56,1	57,9	59,3	58,5	58,9	58,8	58,2	57,9	56,3
		F	1,86	1,92	1,90	1,77	1,86	1,47	1,20	1,17	1,46	1,63
		G	1,94	2,00	1,93	1,63	1,76	1,34	1,11	1,10	1,44	1,55
		Pol_d	53,7	55,1	56,9	58,2	57,4	58,0	58,1	57,5	57,1	55,4
		Pol/S_{gc}	1,00	0,99	0,99	0,99	0,99	1,00	1,00	1,00	0,99	0,99
		Pol/Pol_d ...	1,01	1,01	1,01	1,00	1,01	1,01	1,01	1,01	1,00	1,01
		F/G	0,96	0,96	0,98	1,09	1,06	1,10	1,08	1,06	1,01	1,05
	Molasses	Pol	23,9	22,8	22,7	24,1	23,3	25,9	29,7	27,7	25,7	28,7
		S_{LE}	29,1	28,1	28,3	29,7	28,9	29,7	32,0	30,6	29,6	31,7
		S_{gc}	27,7	27,1	27,1	28,2	27,4	28,1	30,0	28,4	27,5	30,5
		F	10,2	11,0	11,4	10,7	10,0	8,1	6,4	7,0	7,8	8,3
		G	8,8	9,0	9,2	7,7	6,9	5,1	3,9	4,4	5,1	6,3
		Pol_d	20,8	19,2	18,8	19,7	19,2	21,2	24,5	22,4	21,0	24,2
		Pol/S_{gc}	0,86	0,84	0,84	0,86	0,85	0,92	0,99	0,98	0,93	0,94
		Pol/Pol_d ...	1,15	1,19	1,21	1,22	1,21	1,22	1,21	1,24	1,22	1,19
		S_{LE}/S_{gc} ...	1,05	1,04	1,04	1,05	1,05	1,06	1,07	1,08	1,08	1,04
		F/G	1,16	1,22	1,24	1,39	1,45	1,59	1,64	1,59	1,53	1,32
B	Molasses	Pol	–	22,3	21,7	21,8	21,3	22,2	25,9	26,5	25,4	
		S_{LE}	–	27,3	27,0	27,0	27,3	27,9	29,5	30,1	29,8	
		S_{gc}	–	26,3	26,1	26,2	26,3	27,0	27,9	28,4	27,9	
		F	–	9,1	9,6	9,3	10,1	9,2	7,7	7,7	7,7	
		G	–	5,5	5,5	5,5	5,3	4,0	3,2	3,4	3,5	
		Pol_d	–	18,3	17,4	17,9	16,7	17,7	20,0	20,7	20,3	
		Pol/S_{gc}	–	0,85	0,83	0,83	0,81	0,82	0,93	0,93	0,91	
		Pol/Pol_d ...	–	1,22	1,25	1,22	1,28	1,25	1,30	1,28	1,25	
		S_{LE}/S_{gc} ...	–	1,04	1,03	1,03	1,04	1,03	1,06	1,06	1,07	
		F/G	–	1,65	1,75	1,69	1,91	2,30	2,41	2,26	2,20	

Key: S_{gc} = sucrose determined by gas chromatography
Pol_d = Pol derived from sucrose, glucose and fructose (explanation follows in text)
S_{LE} = sucrose determined by Lane & Eynon after acid hydrolysis.
F = fructose
G = glucose

1) Sucrose by Lane and Eynon :

Table 10 illustrates the fact that although the Lane and Eynon chemical method consistently overestimated sucrose, since it includes any non-reducing compounds which yield, after hydrolysis, substances reducing to Fehling's solution, it was a very much better estimate of sucrose than was pol. The mean difference between the Lane and Eynon and g.l.c. methods was 1,4 $\pm$ 0,4 units for the season.

2) Sucrose by Polarisation :

a) Optically-active impurities -

Not unexpectedly the difference between pol and sucrose (by g.l.c.) was large and variable. We have demonstrated considerable changes in both absolute and relative levels of some of the main non-sucrose constituents during sugar boiling, with as much as 34% of the glucose in syrup being destroyed. Such changes in polarising substances will affect the pol in molasses and hence the pol-based factory balance.

Kort et al (11) found no direct correlation between either the level of reducing substances, fructose, glucose or F/G ratios and the difference between sucrose and pol.

The polarising properties of the individual sugars have been well documented and their contribution to the pol can be derived :

$$Pol_{experimental} = Pol_d + Pol_x$$

where

$$Pol_d = Pol_{sucrose} + Pol_{glucose} + Pol_{fructose}$$ (See Appendix 3)

and Pol_x is due to other influences on optical activity.

Pol_d correlated well with pol_{exp}, but showed an off-set of 4 - 5 units :

$$Pol_{exp} = 5,18 + 0,96\ Pol_d$$

(r = 0,97 for 86 molasses pairs)

The correlation confirms that fructose and glucose are the main non-sucrose contributions to pol and underlines the fact that pol is a poor estimate of sucrose for low purity products.

Pol_x was always dextrorotatory and remarkably similar at all three mills (4,0 at EM; 4,4 at ME and 4,8 at mill B and 0,5 units for syrup). By relating pol_x to chloride it was evident that some of this unaccounted pol was formed during sugar boiling (Pol_x/Cl^- : 1,2 for syrup and 2,2 for molasses)

b) Analytical error -

Although most of the difference between pol and sucrose has been explained in terms of the major optically-active impurities, the unaccounted pol still amounts to approximately 0,5 units for syrup and 4 - 5 units for molasses. It is widely acknowledged that many inorganic salts can affect the polarisation of sugar solutions (20) and the effect of basic lead acetate clarification on the polarisation of raw sugars has been discussed by Mesley (31). Influences included the removal of optically-active substances (in particular fructose) from solution as well as altering the rotation of substances (e.g. fructose, amino acids) remaining in solution. The magnitude of the effect depended on both sugar and salt concentration. (11, 20, 31)

To establish how much of the unaccounted pol could be attributed to analytical errors associated with lead clarification several syrup and molasses samples were clarified using the standard procedure (under Experimental).

Solutions of molasses and syrup were analysed for fructose, glucose and sucrose before and after the addition of dry lead acetate. Changes in the amount of glucose relative to sucrose were well under 5% whereas the ratio fructose/sucrose decreased by 16-20%. The derived pol was calculated for the solutions with and without lead acetate assuming this fructose loss to be the only change. Results are summarised in Table 11.

TABLE 11 - Effect of Lead Acetate Clarification on Pol_X

Product	Samples		F : G : S	F/G	Pol_X
Syrup		No Clarification	0,27:0,26:10	1,04	0,6
	5	Clarified	0,22:0,26:10	0,85	0,3
Molasses		No Clarification	0,25:0,18:1	1,39	3,6
	8	Clarified	0,21:0,18:1	1,17	2,1
Refinery Molasses		No Clarification	0,15:0,22:1	0,68	5,7
	2	Clarified	0,12:0,21:1	0,57	4,4

Thus the physical removal of fructose during lead acetate clarification could have inflated syrup pols by about 0,3 units and molasses pols by about 1,5 units. Relative to chloride this was of the order of 0,8 units in both streams.

Hence although pol_X would appear to represent the contribution from optically-active impurities other than fructose or glucose, under our experimental conditions 1,5 units could be due to the effect of lead acetate on the analysis. The residual contribution from other optically-active impurities was about 2,5 - 3,5 units.

CONCLUSIONS

The data presented for two South African cane sugar factories during the 1977-78 crushing season showed that considerable variations in the levels of invert occurred and that the relative proportions of the various non-sucrose constituents in syrup altered during the year. Similar changes were far more pronounced in molasses with the ratio of fructose to glucose increasing in the boiling house - fructose increased, amino-nitrogen dropped by almost one-third and glucose decreased by as much as 35% relative to the levels in syrup.

Limited results on successive boilings indicated that, in the boiling house, hydrolysis was probably the predominant reaction prior to A-molasses, but as boiling continued both glucose and fructose were destroyed faster than they were formed. As glucose was removed more rapidly than fructose, the F/G ratio in molasses was higher than in syrup. However, if sucrose inversion is significant the glucose loss could well be masked. Such conditions would probably also favour fructose destruction so that the ratio of fructose to glucose could then decrease.

Although no direct relationship was established between glucose losses and amino-nitrogen levels, circumstantial evidence indicated a carbonyl-amino interaction (i.e. Maillard reaction). During the 1977/78 season gas was evolved from massecuites at many factories in South Africa. This gassing was most noticeable and most troublesome during the September - October period. Other work in our laboratories (under controlled temperature conditions) showed that some sucrose, some fructose and large amounts of glucose were destroyed when massecuites produced gas.

The imbalance in the amounts of glucose and fructose, coupled with the variable concentrations of these sugars in molasses had the largest effect on the pol result. We found that dry lead acetate clarification inflated optical rotations, which is in agreement with the findings of other authors. The procedure used to assess the effect of lead appears accurate and precise enough to distinguish between physical removal of the monosaccharides and alterations in their optical activities. Further work in this direction might be valuable.

Factory personnel have long maintained that things 'happen' in September - October (this is generally shortly after the start of the Spring rains and overlaps the cane-sucrose maturity peak). We have successfully monitored some of these 'happenings' in the boiling house under processing conditions. If the causes of such effects can be established and adequately explained, we will be in a far stronger position to control the process effectively.

It cannot be assumed that the differences observed in syrup were due solely to seasonal variations in cane composition and not also to some extent to processing variables. We also feel that measuring specific amino-acids may yield more information than the overall figure obtained at present. Current work has been extended to include routine monitoring of fructose, glucose, sucrose and amino-nitrogen in mixed and clarified juices (i.e. prior to the boiling house)

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APPENDIX 1.

Procedure for glucose, fructose and sucrose in factory products.

Materials : Fructose (B.D.H. low in glucose)
Glucose (B.D.H. Analar)
Sucrose (B.D.H. Aristar)
Xylose (B.D.H. Biochemical)
Trehalose (B.D.H. Biochemical)

(Note : All reference sugars were dried in vacuo over phosphorus pentoxide)

Pyridine (Merck for Analysis)
Hydroxylamine hydrochloride (M&B Lab. Reagent)
Dimethyl-amino-ethanol (B.D.H. Lab. Reagent)
Hexamethyldisilazane (HMDS) (Ohio Valley)
Trifluoroacetic acid (T.F.A.) (Pierce)
Benzoic acid (B.D.H. Lab. reagent)

Reagents : A - Sodium benzoate :- 0,3% aqueous solution, pH is adjusted to 6,9 ± 0,1 with sodium hydroxide.

B - Hydroxylamine :- Hydroxylamine hydrochloride (2,5 g) dissolved in pyridine (100 mls).

C - Oximation reagent :- Dimethyl-amino-ethanol (270 µl) is added to reagent B (5 ml) just before use.

Procedure :

1. Preparation of reference sugar solutions -

The following sugars are massed into dry 6 ml hypovials according to the product being analysed and the corresponding amount of sodium benzoate (reagent A) added :

Prepared for :		Syrup	Molasses	
			**(a)	(b)
Xylose	(mg)	* 12 - 20	200	100
Fructose	(mg)	* 12 - 20	220 - 170	125 - 100
Glucose	(mg)	* 12 - 20	180 - 150	100 - 70
Sucrose	(mg)	550 -590	520 - 600	
Trehalose	(mg)	560	520	
Reagent A	(ml)	1,4	2,4	

Notes : * Added volumetrically :- 300 - 500 µl of either

i) 4% xylose or ii) 4% glucose and 4% fructose.

The volume of sodium benzoate added is adjusted so that the total volume added is 1,4 ml.

** a) is used when reducing sugar levels are 12 - 20% and
b) for lower reducing sugar levels.

Calibration standards are prepared so that the sample range is bracketed.

The vials are sealed with parafilm and shaken until the sugars have dissolved.

2. Sample preparation -

Duplicate samples with internal standards are massed into dry 6 ml hypovials and sodium benzoate (reagent A) added :

		Syrup	Molasses
Sample	(g)	0,50	2,00
Xylose	(mg)	* 6 - 10	a) 200 b) 100
Trehalose	(mg)	280	520
Reagent A	(ml)	* 0,5	2,0

Notes : * Added volumetrically :- 150 - 250 µl of 4% xylose solution and the volume of sodium benzoate adjusted so that the total volume added is 0,5 ml.

The vials are sealed with parafilm and shaken until the sugars dissolve.

3. Oximation -

Aliquots (5 ul) of the reference standard and sample solutions are placed in 3 ml screw-cap vials. Oximation reagent (reagent C) (0,5 ml) is added and the vials well shaken at 80°C in an ultrasonic bath (10 mins).

4. Silylation -

The vials are cooled, HMDS (0,45 ml) and TFA (50 ul) added and placed in an ultrasonic bath at 80°C (10 mins). After cooling and allowing the precipitate to settle, the supernatant is transferred to 2 ml hypovials which are then sealed.

5. Gas chromatographic separation -

Separations were achieved using OV-17 as stationary phase. Columns were either packed conventionally or WCOT columns. G.c. conditions are summarised in Table 12.

TABLE 12 -

G.c.	Varian 2700	H.P. 5840
Column	1 metre x 3 mm OD S.S. packed with 3% OV-17 on Chromosorb W (HP) 80/100 mesh	50 metres x 0,5 mm I.D. S.S. coated with OV-17
Injection temperature °C	250	250
Detector temperature °C	300	250
N_2 flow rate	25 ml min^{-1}	Column : 3 ml min^{-1} Vent : 200 ml min^{-1} Make-up: 47 ml min^{-1}
H_2 flow rate	33 ml min^{-1}	39 ml min^{-1}
Air flow rate	500 ml min^{-1}	240 ml min^{-1}
Injection volume	1 ul (manual)	10 ul - split ratio 70 : 1
Initial temperature	120 °C	180 °C
Final temperature	275 °C	250 °C
Programming rate	15° min^{-1}	12 ° min^{-1}
Integrator	HP 3380 S	
Slope sensitivity	0,3 mV min^{-1}	0,3 (G,F) 0,76 (S)

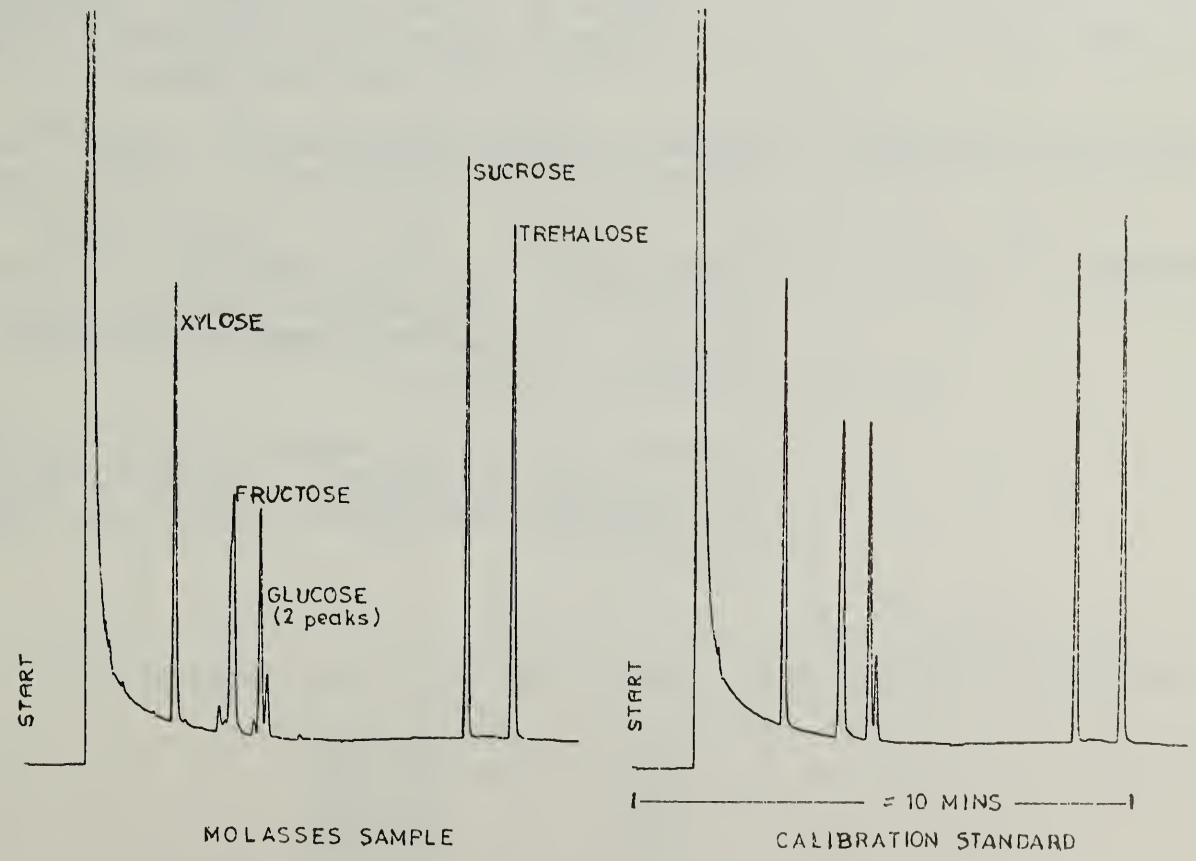

FIGURE 5 - Typical gas chromatograms.

APPENDIX 2.

Procedure for amino-nitrogen in syrup and molasses

Materials :

Ninhydrin (B.D.H. Lab. reagent)
Hydrazine sulphate (M&B Lab. reagent)
Sodium acetate trihydrate (B.D.H. Lab. reagent)
Acetic acid (B.D.H. Analar)
2-Methoxyethanol (Methyl Cellosolve)(Merck for synthesis)
Aspartic acid (B.D.H. Biochemical)
Asparagine (B.D.H. Biochemical)

Reagents :

A - Sodium acetate buffer (pH 5,5) :- Dissolve sodium acetate trihydrate (272 g) in distilled water (200 ml), warming if necessary. Cool and add acetic acid (glacial) (50 ml). Dilute to 500 ml. Adjust pH to 5,5 with sodium hydroxide if necessary.

B - Hydrazine sulphate (2 mM) :- Hydrazine sulphate (0,1301 g) dissolved in distilled water and made up to 500 ml with distilled water.

C - Ninhydrin reagent :- Ninhydrin (1 g) is dissolved in peroxide free methyl cellosolve (10 ml), reagent A (75 ml) added and diluted to 100 ml with distilled water.

Calibration standards : Aqueous solutions containing 1 - 5 ug ml^{-1} of aspartic acid or asparagine are freshly prepared.

Procedure : Syrup samples (1 g) are diluted to 200 mls with distilled water and molasses samples (1 g) to 500 mls. A Technicon AutoAnalyser is plumbed as indicated in Figure 6.

Standards and diluted samples are placed in sample cups and analysed directly. The mean response for asparagine and aspartic acid is used for calibration.

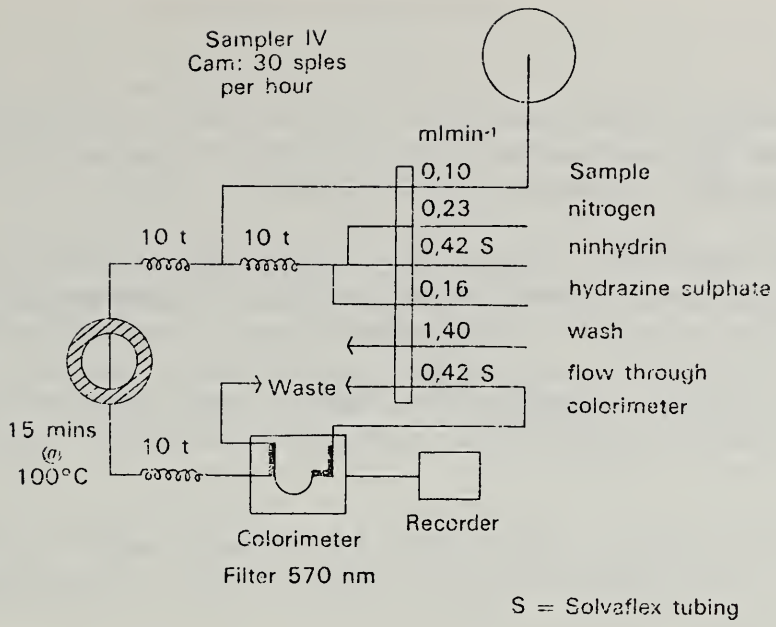

FIGURE 6 - AutoAnalyser manifold for amino-nitrogen

APPENDIX 3.

Calculation of Pol_d

For 26 g of sample dissolved in 100 mls of solution at 20°C and read in a 20 cm polarising tube :

$$Pol_d = \%\ S_{gc} + 0,015\left\{[\alpha]^{20}_{D_G}\%G + [\alpha]^{20}_{D_F}\%F\right\}$$

Values for $[\alpha]^{20}_{D_G}$ and $[\alpha]^{20}_{D_F}$ were

obtained from Bates (32)

$$[\alpha]^{20}_{D_G} = 52,50 + 0,0188\ (\%G \text{ by wt}) + 0,00517\ (\%G \text{ by wt})^2$$

$$[\alpha]^{20}_{D_F} = -\ 88,12 + 0,260\ (\%F \text{ by wt})$$

1% of the major sugars will affect the pol approximately as follows :

Sucrose	+	1,0
Glucose	+	0,8
Fructose	-	1,3
Kestose	+	0,4

M. A. Clarke (CSRRP): I want to congratulate you on some very nice work. You spoke about the seasonal variation in the ratio, with conditions at their worst in October. Is there any rationale for this? Is it changes in cane or temperature, or is what causes this change understood?

P. G. Morel du Boil: We don't know at this stage but we have some ideas. This always comes about two weeks or so after the start of our spring rains. There is evidence in the literature 1/ that during drought conditions there is a build up of amino acids such as asparagine in the cane, and these could undergo a Maillard reaction. If the spring rains didn't come, perhaps the situation would be worse; instead of peaking and coming down it would just go on getting worse.

Another possible explanation is that after the rains come, the cane starts growing again, and forms different amino acids. This is assuming that it is a Maillard reaction, which we don't know.

M. A. Clarke: In work that we have been doing, to be reported in the next two papers, we find a similar situation with the ratio of the reducing sugars: that the fructose exceeds the glucose. However, we have expressed the ratio the other way around, as glucose/fructose, which will not, I trust, cause confusion.

P. G. Morel du Boil: That is what happens when you come from the other side of the world.

J. F. Dowling (Refined Syrups): Most of the time we find dextrose/levulose ratios of 1 or greater, where levulose is destroyed more easily, according to chemistry. Generally the pol is then affected upwards. This occurs in most incoming raw sugars and in most refinery molasses. You have opened up a question for a lot of thought. Most of the work is now over 10 years old, maybe some things have changed. The sucrose by pol and true sucrose by G.L.C. got closer together as you went on in the season, yet the levulose/dextrose ratio went up. That means that there was more levulose, so the pol was more to the left so it should have gotten further away. How can you explain that?

P. G. Morel du Boil: The thing is that we have a very large drop in absolute levels of glucose and fructose through the season. It is the absolute level that affects the pol to a greater extent than the ratio, and since we have far fewer impurities and a far greater proportion of sucrose this now has the overriding effect on the pol. As the cane matures, the invert drops off dramatically. This can be seen in Table 4 or Figure 4 where fructose and glucose levels for syrup at Mount Edgecombe in November are about half those in May.

1/ Wiggins, L. F. and Williams, J. J., Ag. and Food Chem., 3 (4), 341, 1955

J. F. Dowling: Have you compared sucrose by GLC with sucrose by isotope dilution?

P. G. Morel du Boil: No, not during this particular project. However, we have previously compared the two methods in collaboration with the SMRI. In all cases the isotope dilution method gave results about 0.5% higher for sucrose in molasses. The difference has been attributed to the difficulty of isolating pure sucrose free of co-precipitated impurities. It is worth noting that at the latest ICUMSA meeting ID results were treated far more cautiously because of this problem of isolating uncontaminated sucrose.

M. C. Bennett (Tate and Lyle): I too would like to congratulate you on a very nice presentation. My question concerns something perhaps specific to your part of the world. I am aware that the Sugar Milling Research Institute carries out routine comparisons of factory performance throughout South Africa. Do you already know what impact your analytical procedures have on interfactory comparisons which tend to mean so much in your country?

P. G. Morel du Boil: We have been doing sucrose analyses using G.L.C. at two of our mills over the last few crushing seasons. Variations in many of the performance values can be attributed to the inaccuracy of direct pol for measuring sucrose. As we have seen, the polarising properties of the non-sucrose alter during processing. This, in turn, leads to errors in pol balances. Generally, factory balances are a lot more equitable if you use true sucrose rather than pol. Overall performance yardsticks that adjust for impurity content are particularly affected by differences between pol and sucrose so that boiling house recoveries, for example, are not as different between mills when using true sucrose.

F. G. Carpenter (CSRRP): This brings to mind a problem that was found in the U. S. a few years ago. The cane breeders had developed a new variety of cane which had very high pol. After a few years, enough was growing in one area so that one day one mill got nothing but this variety and they got far less sugar than expected. It was suspected that what the cane breeders had been breeding was pol not sucrose. What you have here is a method of avoiding this pitfall of false pol.

N. I. James (USDA): Yes, that was an L variety developed at Louisiana State University, not a USDA variety, but it did stimulate considerable activity in using other methods for what we were condidering to be sucrose. It turned out that the major problem was low extraction rather than false pol, but it could have been a false pol problem.

P. G. Morel du Boil: We have been using G.L.C. for the determination of sucrose in our mixed juices quite routinely. At our Mount Edgecombe factory, which has higher invert levels than most of our other mills, the difference between pol and sucrose is fairly marked. Here, the ratio of pol to sucrose is about 0.98 - 0.985 instead of 0.995 or greater as it is as at most other mills.

SUGARS IN MOLASSES

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ABSTRACT

A high pressure liquid chromatography (HPLC) method developed for sucrose, glucose and fructose has been applied to a variety of molasses samples. Techniques for applying HPLC analysis to molasses are discussed. The results are compared to results by classical analytical methods. The observation that glucose/fructose ratios were frequently less than unity is discussed.

INTRODUCTION

The estimation of absolute and relative quantities of sucrose, glucose and fructose in molasses has been an important problem to the sugar industry for many years. The sugars in molasses have been lost to sugar production; the greater the quantity of sugars in molasses, the lower the yield of the refinery or factory. Some sugar must necessarily be lost to molasses; this amount is determined by the non-sugars content of the molasses, and the melassigenic quotients of those non-sugars. It is sugars in excess of this amount that represent a lowered yield.

These quantities of sugars in molasses are also important in trading: molasses is bought and sold on the level of total sugars it contains.

From a technical point of view, the relative amounts of these sugars can indicate reactions that took place in sugar liquors, particularly during the crystallization that left the molasses as a byproduct. Knowledge of the individual sugars is important for investigation of their reactions with other constituents. It is also significant in the burgeoning field of fermentation products.

The sugars considered in this study are sucrose, glucose and fructose, the sugars of commercial importance in molasses. Also present in molasses are other mono-and disaccharides, and some trisaccharides and oligosaccharides. It is because of the complex composition of molasses that analysis of the sugars there is so difficult. Traditional optical methods work poorly, because of the many optically active compounds in the sample substance. Similarly, oxidation and reduction methods lack accuracy because there are many other reducing compounds

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*This work was done in cooperation with the Southern Regional Research Center, SEA, USDA.

present as well as glucose and fructose. In comparison of analyses of sugar in molasses by isotope dilution, gas liquid chromatography, chemical methods and polarization, it was concluded that the pol data gave no useful information (8).

There are various types of molasses, classified by their origin and sugar content. Blackstrap molasses, the byproduct of either raw cane sugar factories or cane refineries, diluted to a standard Brix, was used in this study. The samples were from a variety of origins. Blackstrap, as defined by the Association of American Feed Control Officials (1), "must not contain less than 46% total sugars, expressed as invert, and be not less than 79.5 Brix by double dilution." Most blackstrap is sold for animal feed. Beet molasses, which contains much less invert than cane, was not considered here, nor was high-test molasses, which is actually a heavy, partially inverted cane syrup, made from either cane juice or refinery syrup.

There has been a great deal of work in this area of sugars in low purity materials over the years. When the errors inherent in polarization and reducing methods became obvious, paper chromatographic analyses were tried (5,6), with colorimetric identification of the sugars, but quantitation was poor, and develment time to allow good separation of the sugars was rather long (up to 48 h). Separation of the three sugars on columns of granular carbon (12) or carbon-filteraid mixtures (10), with subsequent individual analyses worked very well, but involved several detailed analyses - an enzyme method for glucose and, in the former case, a colorimetric analysis for fructose. Gas-liquid chromatographic methods were tried (4,13), but at first gave difficulties with quantitation, especially in molasses. These problems with GLC have been solved, but preparation of derivatives, with the attendant question of completeness of derivatization, is still required.

The ratio of glucose to fructose in molasses and other sugar products has been the subject of much discussion. With regard to polarimetric measurements, if the ratio is greater than 1, i.e., if there is more glucose than fructose, the polarization will be higher than that due to the actual sucrose, and if the ratio is less than 1, lower. The literature generally shows a ratio of greater than 1 in refinery liquors (6,12) and either greater or, more usually, less than one in cane molasses (5,6,8-11). Since fructose is more reactive under alkaline conditions, and glucose under acid, it might be expected that factory molasses should have a G/F ratio less than one, and refinery molasses greater than one, but no such clearly defined situation apparently exists. There have been problems in methodology that may have confused the ratio question: in many studies (10), fructose has been found by difference between glucose and reducing sugars, thereby incorporating error due to reducing substances.

Irvine's work on cane juice (7), with GLC methods, showed that the ratio in sugarcane and juice is generally greater than 1, ranging from 1.3 to 2.8. Raw sugars also generally exhibit a ratio greater than 1 (12). A recent study by Mauch (9), using the enzymatic-colorimetric determinations with hexokinase and other enzymes, found an average ratio of approximately 1 in cane molasses, although more samples had a ratio below 1 than above. The age and storage conditions of these samples is not known. Work in South Africa, comparing different types of analyses of sugars in molasses (8), showed a G/F ratio of less than 1 for all samples, analyzed by gas liquid chromatography.

For these reasons: specific determination of sucrose in molasses and comparison to determination by optical methods, and the specific determination of glucose and fructose and their ratio, it was decided to analyze a series of cane molasses samples by high pressure liquid chromatography (HPLC). This technique has been used with success in this laboratory for analyses of sugar mixtures (2). HPLC will give specific results for sucrose, glucose and fructose, in a rapid, accurate and reproducible analysis. The problem of HPLC column deterioration from salts and high molecular weight compounds in the molasses was solved by ion-exchange resin treatment and filtration, after ascertaining that such treatment did not remove sugars from the sample.

MATERIALS AND METHODS

The molasses samples were kindly supplied by the U.S. Customs Service Laboratory, New Orleans, and the New York Sugar Trade Laboratory, Clark, New Jersey. After analysis at their respective laboratories, the samples were kept chilled or frozen until they were analyzed by HPLC, including during their period in transit.

A sample of approximately 20 g of molasses was weighed out and diluted to approximately 200 g with deionized water. Although only a few milligrams were actually required for the HPLC analysis, a large sample was taken for the dilution to minimize error in sampling. Each molasses was thoroughly mixed in its container before the sample was removed.

The densities of the approximately 10% solution were taken, i.e., a discrete volume of solution was accurately weighed, or alternately, a 20 g sample of molasses was dissolved and quantitatively made to 200 ml volume.

Sample Cleanup. The packing material in carbohydrate analysis columns is gradually destroyed by salts and high molecular weight compounds. Although frequent washing minimizes the damage (2), it is irreversible and causes change in the resolving power of the column. The best procedure is to remove the harmful materials from the sample before injection.

To accomplish this, the molasses solutions were treated with anionic and cationic ion exchange resins. Suitable quantities of Amberlite CG-400 strong base anion exchange resin, OH form, 200-400 mesh, and CG-50 weak acid cation exchange resin, H form, 200-400 mesh (Rohm and Haas Co., Independence Mall W., Philadelphia, PA 19105) were washed with deionized water and then with methanol, and then air-dried over a vacuum filter for 24 h. To about 40 ml of each sample solution was added 5 ml of each dry resin. The mixture was stirred, and the resins filtered off on a vacuum filter. The fine mesh size of the resins has the effect of absorbing some high molecular weight material in the sample. The deionized sample was filtered through a 5 μm Millipore filter (fluorocarbon) in a Swinney adapter, before an aliquot was injected into the chromatograph.

HPLC. Analyses were carried out using a Waters Associates (Waters Associates, Milford, Mass. 01757) Model No. ALC/GPC 244 chromatograph, with Model 6000A pump, U6K injector, and R401 differential refractive detector. The column was a Whatman PXS10/25PAC, bonded cyano-amino type polar phase column, for carbohydrate analysis (Whatman Inc., 9 Bridewell Place, Clifton, N.J. 07014). Chromatograms were displayed on a Honeywell Electronik 194 Recorder. (Honeywell Inc., Fort Washington, PA 19034). Flow rate was 1.5 ml/min, of a solvent mixture

of 83 ml acetonitrile to 17 ml water. In solvent preparation, deionized water was passed over a column of strong base anion exchange resin in the OH form, and then over a column of strong acid cationic resin in the H form, and then over a column of activated granular carbon, to ensure removal of salts, organics, and microorganisms. Solvents were mixed, and filtered through a 5 μm Millipore fluorocarbon filter, and sonicated for 10 min.

Sample and standard injections, usually of 10 μl, were delivered by Pressure-Lok syringes (Precision Sampling Corp., Baton Rouge, LA 70895), and run at an attenuation of 8. Details on preparation of standard solutions, and complete details on chromatographic procedure, may be found in an earlier publication from this laboratory (2).

The column was washed with a 50% methanol-water mixture after each day's use, and stored in this mixture overnight. For longer storage times, this column is stored in hexane, with intermediate solvents of methanol and then chloroform because of miscibility requirements.

Calibration. Standards were run such that there was one standard of higher and one of lower concentration than each sample, within a ± 2 mg/ml range (2). Each sample concentration was read from its two-point calibration, and the concentration of sugar in molasses was calculated as a percentage of the original weight of the molasses, including in the calculation the density factor for the dilute molasses solution, if necessary.

RESULTS AND DISCUSSION

Sample Treatment

It has been recommended by the manufacturers of carbohydrate analysis columns that any sample of sugars or process liquors that might contain salts or deterioration products should be cleaned up by treatment with a precolumn. A precolumn, of about 1" in depth in a micropipette, of Corasil/AX Bondapak, (Waters Associates), strong anion exchanger packing material nad been used in earlier work on HPLC of sugars (2). This treatment was effective in extending the life of good column performance, and it did not cause loss of sugars by adsorption, that is, not more than was allowed by normal experimental error. The Corasil/AX material, however, is expensive ($125 for 15 ml), and it was thought possible by the authors that a similarly effective, but cheaper, material could be found. It was found that Amberlite CG-400 resin, 200-400 mesh, a strong base anion exchange resin, when in the OH form was equally effective as a precolumn material, and that sugar loss by adsorption was again not significant. For the molasses samples, it was thought necessary to use a cation exchange resin also, and Amberlite CG-50, weak acid cation exchange resin, 200-400 mesh, H form, proved suitable. Because the molasses sample solutions are of higher viscosity than normal sugar samples, the time taken to run the sample over two fine mesh resin columns was impractical for efficient procedure. The column is first washed with two bed volumes of sample solution, and the ion-exchanged sample is then collected. There was also an increased probability of loss of sugars by adsorption, with two columns of resin. So, the procedure described in the "Methods and Materials" section, adding dry resin to sample solution, was adopted. Tests for sugar loss by adsorption on the added fine mesh resins showed that loss was again within experimental error.

Table 1. Concentrations of sucrose in molasses samples

Sample	Sucrose, HPLC	Sucrose, double pol	Diff.	Total sugars, HPLC	Total sugars, classical
1	29.90	36.2	-6.30	44.44	54.3
2	28.05	36.7	-7.65	42.33	56.7
3	27.26	34.0	-6.74	41.51	54.2
4	26.46	34.1	-7.64	39.54	56.7
5	28.10	35.2	-7.10	40.54	55.6
6	30.27	36.9	-6.63	43.10	56.0
7	26.71	34.1	-7.39	36.68	49.4
8	28.63	37.8	-8.17	42.82	57.9

Correlation coefficient for sucrose by HPLC with sucrose by double pol:
r = +0.94

Concentrations of Sugars

The concentrations of sugars in two series of molasses samples are shown in Tables 1 and 2, and 3 and 4. Results from analyses by classical methods are also shown. In the first set, sucrose was determined by double polarization, with acid inversion (3), and reducing sugars by a Lane-Eynon titration (3). In the second set (samples 9 to 14), sucrose was again determined by a double polarization, and reducing sugars by the gravimetric Munson and Walker copper reduction method (3).

According to tables 1 and 3, the sucrose determined by HPLC - or the so-called true sucrose - is from 4.42% to 10.30% lower than the sucrose shown by a double polarization measurement with acid inversion.

In the double polarization, everything that is broken down or inverted by acid treatment to produce a compound that will polarize light is read as sucrose, with limited corrections. The results shown herein indicate that in molasses samples, there are considerably more compounds than sucrose that cause the dextrorotation of light after acid treatment. The problem of the G/F ratio comes into this calculation: in the original polarization, the calculation is based on a 1:1 mixture of glucose and fructose, whereas the ratio in actuality ranges from 0.6:1 to 1.15:1. In the general situation where G/F < 1, insufficient allowance is made for the levorotatory effect of fructose, and the reading indicates less sucrose than is actually present. After acid inversion, when the contribution made by the excess fructose has a smaller effect on the

Table 2. Concentrations of fructose and glucose in molasses samples

Sample	Fructose, HPLC	Glucose, HPLC	Total	Reduc. sugars (Lane-Eynon)	Diff.	Ratio G/F
1	8.28	6.26	14.54	18.1	-3.56	0.76
2	7.34	6.94	14.28	20.0	-5.72	0.95
3	7.75	6.50	14.25	20.2	-5.95	0.84
4	6.56	6.52	13.08	22.6	-7.52	0.99
5	7.36	5.08	12.44	20.4	-7.96	0.69
6	7.72	5.11	12.83	19.1	-6.27	0.66
7	5.75	4.22	9.97	15.3	-5.33	0.73
8	7.90	6.29	14.19	20.1	-5.91	0.80

Correlation coefficient between glucose and fructose by HPLC and reducing sugars by Lane-Eynon: $r = +0.56$

Table 3. Concentrations of sucrose in molasses samples

Sample	Sucrose, HPLC	Sucrose, double pol	Diff.	Total sugars, HPLC	Total sugars, classical
9	25.27	29.69	-4.42	50.36	59.00
10	26.79	35.44	-8.65	43.30	57.61
11	30.49	39.38	-8.89	43.08	54.32
12	28.02	33.02	-5.00	51.63	60.76
13	29.68	39.98	-10.30	41.83	54.81
14	30.72	39.98	-8.66	46.63	60.65

Correlation coefficient between sucrose by HPLC and by double pol: $r = 0.92$

Table 4. Concentrations of fructose and glucose in molasses samples

Sample	Fructose, HPLC	Glucose, HPLC	Total HPLC	Reduc. sugars Munson-Walker	Diff.	Ratio G/F
9	11.69	13.40	25.09	29.31	-4.22	1.15
10	9.17	7.34	16.51	22.07	-5.56	0.80
11	6.62	5.97	12.59	14.94	-2.35	0.90
12	11.20	12.41	23.61	27.54	-3.93	1.11
13	6.82	5.33	12.15	14.83	-2.68	0.78
14	8.65	7.26	15.91	21.27	-5.36	0.84

Correlation coefficient between glucose and fructose by HPLC and reducing sugars by Munson-Walker: r = 0.98

calculated overall polarization, the difference between 2nd and 1st polarization will therefore be greater than it should be, and will indicate a greater amount of sucrose than is actually present.

The large correlation coefficients, r = 0.94, and r = 0.92, so close to 1, for the dependency of values of sucrose calculated by double pol upon the true sucrose indicates that there is a fairly constant error in the sucrose pol measurement. The error is always in the same direction. It is interesting to observe that for molasses with a G/F ratio greater than the double pol reading is closer to the true sucrose. In Tables 3 and 4, in two cases, 9 and 12, the G/F ratio is greater than 1, and the true sucrose (HPLC) values for these two samples are indeed closer to the results for sucrose by the double pol analysis. For example 9, G/F = 1.15, difference in sucrose analyses = 4.42, and for sample 12, G/F = 1.11, and difference in sucrose analyses = 5.00, compared to the average difference over the other 12 samples of 7.90. There is no excess fructose in these samples to cause an increase in the negative error of the initial polarization reading. The error due to the non-unity of the G/F ratio is not the only one in the double pol reading. The breakdown of trisaccharides and oligosaccharides creates another major error in the measurement after acid treatment.

In any discussion of the G/F ratio, or of sucrose levels, microbiological contamination must be considered. No survey has been made for microorganisms in this study, although there has, in all probability, been some activity in these molasses at some point in time. The cold storage of these samples eliminated microbiological activity between the two test times. Since there are such a variety of microorganisms that are specific for either glucose or fructose, it is unlikely that most samples of molasses, including many others we

have analyzed that are not included in this report, would have been contaminated only with glucose specific organisms, creating in most cases, a G/F ratio of less than 1. The samples that show G/F > 1 have very high invert and low sucrose contents. A lot of inversion of sucrose may have occurred shortly before analyses, with too little time to permit much subsequent degradation of glucose. It is much more likely that reactions in the molasses - and in other sugar liquors of similar pH and non-sucrose makeup - consume glucose more than fructose. The Maillard group of reactions is an example.

The results from glucose and fructose measurements by HPLC compared to those from the reducing sugars titration emphasize the unsuitability of the latter for invert sugar analysis in molasses. The low correlation coefficient, r = 0.56, corroborates this. There are many substances, both organic and inorganic, in molasses that can reduce copper as well as fructose and glucose. Apparently the large inconsistencies were not present with the Munson-Walker analysis.

CONCLUSIONS

Results for sucrose determined by high pressure liquid chromatography show values consistently lower than the double pol values, by an average of 7.40% sucrose (s.d. 1.7). Results for glucose plus fructose by HPLC show values lower than those by copper reducing methods, but with a wide range of differences: the average difference is 5.17% (s.d. 1.65). It is apparent that the copper reduction determination does not give reliable or consistent results in molasses, presumably because there are so many other reducing substances present in addition to glucose and fructose.

In the sucrose determination by double pol, additional errors arise from the acid hydrolysis of trisaccharides and higher molecular weight saccharides, which break down to components that affect the optical rotation, apparently in a positive manner like glucose. There is some consistency in the error due to reducing sugars: since the G/F ratio is less than 1 in most cases, there is a consistent lowering of the initial polarization.

The ratio of glucose to fructose is less than 1 in most samples observed. It is interesting that, in earlier work using the HPLC technique to study sucrose degradation in almost pure sucrose solutions, as degradation progressed, the G/F ratio became slightly greater than 1. It appears that in the case where there is a very small concentration of impurities and degradation products, fructose is consumed (or reacts) more quickly than glucose, whereas in low purity liquors, the reverse is true. Since the pH was in the same range (about 5) in both cases, this observation may indicate a direction to follow in the search for sucrose degradation products that show the type and quantity of degradation, and may serve as indicators for sucrose loss in process. Such compounds, when identified, will act as markers to indicate sucrose loss.

The fact that the true sucrose in molasses is rather lower than the double pol value emphasizes the importance of exhaustion of molasses, and could affect calculation of losses, although in this case, this is of more concern to raw sugar mills than to refineries, and depends on how a sugar balance is calculated.

The HPLC determination of sugars in molasses and low purity liquors is a rapid, reliable and reproducible analytical method, particularly in comparison to those methods in current use. Any laboratory already using HPLC should consider this method, with, probably, a column reserved for use with molasses alone.

In future work, this method will be used to determine sugars in following sucrose decomposition in refinery liquors of low purity, in the search for compounds that can be used as tracers for sucrose loss.

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DISCUSSION

R. Moroz (Revere): Why did you use the Whatman column instead of the Waters recommended column?

M. A. Brannan: The Whatman column is not as sensitive as the Waters column. For molasses work this is more of an asset than a detriment, because it is not as affected by the many extraneous materials in molasses. Also, the Whatman is less expensive: $275 as compared to $350.

R. Cormier: (Redpath): Have you tried to make use of the internal standard method?

M. A. Brannan: Yes, we tried that and the different ratios of standard to sugars did not give consistent results. It depended on the concentration of the sugars and the amount of standard. There were too many variables. It did not work. This work is reported in an earlier paper of ours.[1/]

R. Cormier: Is the raffinose the source of any problem in quantifying the sucrose peak?

M. A. Clarke (CSRRP): The raffinose peak comes out after the sucrose but we have not measured it at all. There is very little raffinose in cane sugar.

R. Cormier: It seems that the sucrose peak is free from interference from raffinose. I would guess it is also free of fructose anhydride and other similar carbohydrate interferences. You see, in our case, this is a problem when we use an Aminex Q-15 column, but the mechanism of separation there is different from yours.

1/ Clarke, M. A., Brannan, M. A., and Carpenter, F. G. 1978. Sugar losses by inversion. Proc. Sugar Ind. Technol. In Press.

M. A. Clarke: The fructose anhydride is a separate peak that comes out after sucrose, but closer to sucrose than the trisaccharides. We have not found anything that interferes with the sucrose peak. There are some rare monosaccharides that, if they were there, could interfere with glucose and fructose, but we have been lucky enough to avoid those. The Aminex columns that you mention separate compounds in reverse order to this column; on Aminex, the high molecular weight components elute off first. There may be interference there with sucrose from fructose anhydride and other compounds--I am not well acquainted with that set-up.

R. Cormier: Has the pH been found to have any effect on the resolution of glucose and fructose peaks?

M. A. Clarke: The HPLC columns work best at neutral pH. If you put on samples at pH 3 or 4, you won't put on very many because you will lose your column. The packing material will degenerate and lose separating power. You really can't study any effect of pH on resolution directly.

R. Cormier: What is the pH of the deionized water you used? In our case it is around 5 and that affects the resolution we get when doing analysis with an Aminex WX-4 (Calcium form) column where a correct pH appears to be very important.

M. A. Clarke: The pH of our deionized water also is sometimes less than 7, but we have found no problems with resolution on our columns, although as I mentioned, lower pH is detrimental to the packing material.

M. A. Brannan: Snyder and Kirkland[2/] have a series of standard resolution curves. Our glucose-fructose curves represent about 95% resolution.

J. F. Dowling: (Refined Syrups): When you started out with pure dextrose or pure levulose did you measure the recoveries?

M. A. Brannan: We did not evaluate recoveries of glucose and fructose. We did, however, evaluate recovery of sucrose.

J. F. Dowling: Did you invert pure sucrose and find the D/L ratio? According to previous work, most of the time you will find more dextrose, because levulose is destroyed. If you take commercial medium invert sugars you should find more dextrose than levulose.

When you run a GLC you get two isomers for levulose. Perhaps with HPLC you only see one isomer of the levulose.

2/ Snyder. L. R. and Kirkland, J. J., Modern Liquid Chromatography, Wiley, New York, 1974

M. A. Clarke: To answer your second question first: There is only one peak for levulose (or fructose) and one for glucose on HPLC.

We did not run recoveries per se of glucose and fructose, but we did check standard solutions of glucose and fructose with the ion exchange treatment to see if we were losing any there, and found that we were not. We have the original weights, and the weights that show up on HPLC; so, we have, effectively, recoveries although the samples were not run for that purpose. We did run recoveries for sucrose, which are reported in the next paper.

In the paper presented to SIT last May[1/] results are shown where we inverted sucrose and analyzed for the invert under various conditions of time, temperature and pH. In high purity liquors you do see more glucose and less fructose. This is the unusual situation here: in molasses and lower purity liquors, the G/F ratio is usually less than one, and there is more fructose than glucose.

J. F. Dowling: Did you check your results for sucrose by the isotope dilution method?

M. A. Brannan: No. But that method usually gives a high reading for sucrose.

P. A. Morel du Boil (Huletts): Because of the difference in optical activities of glucose and fructose the pol effects are going to cancel out at about a ratio of 1.6 rather than 1. Although the rotations are opposite, they are not identical.

A. L. Cummings (Nat. Bur. Standards): A 50/50 glucose/fructose mixture will rotate about -0.3 times the rotation of the same amount of sucrose. You mentioned that the classical reducing sugar methods find about 5% more invert than HPLC, and the pol finds about 7% more sucrose than is actually there. Part of the 7% sucrose error could arise from the mathematical treatment of the optical rotation. If you correct the optical rotation for the invert rotation, and think there is more invert there than actually is there, you will get an excessively large positive rotation correction. However, if the invert is really 50/50, the rotation correction error is smaller than the invert content error by a factor of 0.3.

J. E. Morton (Redpath): You gather from Richard Cormier's comments that we are heavily involved in HPLC ourselves. As Richard's associate I am very heartened by what appears to be confirmation of what we feel ourselves. In fact, with regard to your comment in the conclusions that this is a rapid, reliable, reproducible analytical method, we couldn't agree more. And I believe that we are quite near to doing exactly as you suggest. Meanwhile, particularly as you show in your conclusions, and in the paper, in view of the dramatic difference between the two methods, HPLC and the conventional, could you comment on whether the low results for true sucrose in molasses really means that the losses may be very different from what people think.

M. A. Brannan: We can not yet say for sure. Our samples have all been obtained from service laboratories. The analyses in the service laboratories were made an undetermined time after the samples left the sugar mills or refineries. After the service laboratories made their analyses, the samples were frozen and shipped immediately to us. We then analyzed them by HPLC, thawing the samples immediately before analysis. So we know our analyses are comparable to the conventional analyses made in the service laboratories. But some decomposition almost certainly has occurred in the molasses from the time they were made in the mill or refinery until these comparable analyses were made, so that the sugar shown to be in these samples are not the same amounts that were there when the molasses left the factory.

F. G. Carpenter (CSRRP): In most refineries, the molasses is a relatively small stream, and if some analytical error occurs here it is not a big item in the sugar balance. It will be some little correction in the known sugar losses.

However in the raw sugar mill, the largest sugar loss is to molasses and an analytical error here will really change the sugar balance. This will cause some recalculation and rethinking. Pam Morel du Boil in her paper indicated that by using a uniform method throughout the South African cane district, some of the mills that appeared to be good were really no better than all the others.

We are getting better, more realistic, more truthful figures for sucrose, which may not suit those whom the truth hurts.

SUCROSE LOSSES THROUGH DECOMPOSITION IN REFINERY LIQUORS

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ABSTRACT

Sucrose decomposes under acid conditions to invert sugar and subsequently to organic acids and other compounds, and under basic conditions to a range of alkaline degradation products. High pressure liquid chromatographic analysis is used to follow sucrose levels and the manufacture and destruction of invert throughout the refining process.

INTRODUCTION

Sucrose loss, particularly chemical loss, is the subject of an ongoing study by this laboratory (4). Techniques for the analysis of the sugars sucrose, glucose and fructose have been worked out using high pressure liquid chromatography (called HPLC), and losses under laboratory conditions have been determined for the acid pH case (2,3,4).

Sucrose decomposition is responsible not only for the loss of sucrose in process, but also for the formation of many colorant compounds, organic acids, and other non-sugars that must be removed in process. The problem of chemical sucrose loss is double-edged: sucrose is lost, and undesirable organics are formed.

There are several general areas into which these decomposition reactions of sucrose may be divided: inversion is one such area. Under acid and slightly alkaline conditions, sucrose breaks up into glucose and fructose. These monosaccharides can react further to form a great variety of organic acids, aldehydes, ketones and alcohols, many of which contribute to brown or yellow color. The reducing sugars can also react with any amine compounds - this can happen over a wide pH range, but especially readily at acid pH - to form colored compounds, sometimes of high molecular weight. In neutral or alkaline conditions, in addition to Maillard reactions another set of color-forming reactions, the alkaline degradation of fructose, comes into effect (1,7,9). Sucrose is most stable to decomposition between pH 8 and pH 9 (1).

All these decomposition reactions proceed more quickly at higher temperatures. Solutions of raw sugar under refining conditions provide good conditions for many of these reactions to take place. Because of the variety of types of reactions, and of conditions at refinery processing steps, it was decided to examine samples of refinery liquors to determine where the

greatest losses occur. The HPLC method is appropriate for this study because samples can be analyzed directly in water solution, after dilution and Millipore filtration, and because this analysis gives separate and specific readings for glucose, fructose and sucrose (2,3,4,5,8).

There has been no attempt made to work out a mass balance in this study. Each individual plant will be different, and will indeed differ from day to day. The goal in this survey is to look at each step in the refinery as a unit process, and to look at what happens to sucrose, fructose and glucose in each operation.

MATERIALS AND METHODS

Samples: Samples were obtained at many different processing steps from two refineries that use carbonatation defecation and bone char decolorization. Samples obtained and those analyzed thus far in this study are shown in table 1. Additional analyses will be reported in a future publication. Samples were composite samples over any one day, and composite sets for several days are reported here. Samples were frozen as soon as they were removed from process, to prevent further decomposition or microbiological action.

Table 1. Refinery samples obtained and analyzed.

Sample	Analysis run
Raw sugar	x
Centrifugal wash water	
Washed sugar liquor	x
Affination syrup	
Melter water	
Melt liquor	
Remelt liquor	x
Carbonated liquor before filtration	
Press-filtered liquor	x
Liquor off char	x
Heavy No. 1 liquor	x
First strike sugar	
Second strike magma and syrup	
Third strike magma and syrup	

Sample preparation: For solid sugars, 20 g of sugar was dissolved in dionized water, and made up to 100 ml in a volumetric flask. This solution was used for glucose and fructose analysis. A 5 ml aliquot of this solution was further diluted volumetrically to 50 ml, for analysis of sucrose, the more concentrated sugar. For heavy liquors, 5 g of the liquor (all were approximately 60 Brix to 65 Brix) was diluted to 25 ml, volumetrically, for determination of glucose and fructose, and a 5 ml aliquot of this solution was further diluted to 50 ml for analysis of sucrose.

Sample clean-up: In an earlier publication (4), the use of pre-column of a strong anion exchanger column packing material was described. This pre-column was very effective in removing organics and salts that caused deterioration of the carbohydrate analysis column, but the material was expensive. An attempt to substitute a strong base anion-exchange resin, of 200-400 mesh (chromatographic size) proved successful: the resin removed the harmful compounds, but did not absorb sugars beyond the limits of experimental error. So, two pre-columns were used: first, a column of Amberlite MB-3, indicating mixed-bed resin, 20-50 mesh, and then a column of Amberlite CG-400 strong base anion-exchange resin. Each pre-column was about 1 inch depth in a micropipette. The resin column was washed with three bed volumes of sample solution before a sample was collected for injection. Fresh pre-columns were used for each sample solution. The sample was then filtered through a syringe fitted with a Swinney adaptor holding a 5 μm Millipore fluorocarbon filter, before injection.

HPLC: All analyses were carried out using a Waters Associates (Waters Associates, Milford, Mass. 01757) Model No. ALC/GPC 244 chromatograph, with Model 6000A pump, U6K injector, R-401 differential refractive index detector, and μBondapak-carbohydrate column (30 cm x 4 mm i.d.), connected to a Honeywell Electronik 194 recorder. Flow rates were generally 1.5 ml/min. Injection volume was generally 10 μl for sucrose, and 25 μl for fructose-glucose samples, depending on sample concentration, delivered by Pressure-Lok syringes (Precision Sampling Corp., Raton Rouge, LA 70895).

Solvents: Organic solvents used were Burdick and Jackson Distilled in Glass (Burdick and Jackson Labs., Muskegon, Michigan 49442). Deionized water was passed over a column of strong base anion exchange resin in the OH form, then over a column of strong acid, cationic resin in the H^+ form, and then over a column of activated granular carbon, to ensure removal of salts and organics. A solvent mixture of 83 ml acetonitrile to 17 ml water was used for all analyses. The solvents were mixed, filtered through a 5.0 μm pore size Millipore fluorocarbon filter, and sonicated for five minutes. (Disontegrator Model, Ultrasonic Industries, Inc., Plainview, N. Y.). During operation of the chromatograph, the Model 440 UV detector was kept running to monitor the solvent for impurity.

Calibration: The method of bracketing each sample with standards of higher and lower concentrations was used (4). Since glucose-fructose and sucrose were run separately because of their very different concentration ranges, this meant that four standards and two unknowns were run for each sample.

Accuracy and precision: In order to ascertain the accuracy of the method, recovery studies were made. A standard of known concentration of sucrose was

run under the usual conditions of solvent mixture, flow rate, attenuation and sample size. A known weight of sucrose was added to the standard solution, and the new fortified solution was run. For each of these, two standards, one of higher and one of lower concentration, were run using the method of bracketing to get the experimental value for the initial and fortified concentrations of sucrose, and the known weight of added sucrose was compared to the experimentally calculated weight from the chromatograms.

Brix: Refractometer Brix readings were made on the sample (Abbe' refractometer, Carl Zeiss, Germany), and corrected to 20° C, to give some comparative value for the sucrose analyses.

RESULTS AND DISCUSSION

Results on the recoveries of sucrose showed a mean value for recovery of 99.93% ± 1.2%. On repeated analysis of known solutions, the accuracy of a single (as compared to the two values calculated in the recoveries) HPLC value compared to the known concentration, was 100.9% ± 0.65%. The coefficient of variation on these readings was an extremely good 0.65%.

Table 2. Analysis of raw sugar and refinery liquors

Sample	Brix	pH	%Sucrose	%Fructose	%Glucose	Brix - sucrose	Sucrose / Brix
raw sugar	97.59 (pol)		98.84	0.26	0.30		
washed sugar liquor	65.5	7.75	63.16	0.04	0.02	2.34	0.9643
melt liquor	66.0	7.45	63.83	0.02	0.02	2.17	0.9671
set B							
raw sugar	98.03 (pol)		97.75	0.02	0.18		
washed sugar liquor	65.75	8.00	64.73	0.02	0.02	1.02	0.9845
melt liquor	66.2	7.45	64.31	0.02	0.02	1.89	0.9715
set C							
raw sugar	97.6 (pol)		97.50	0.38	0.30		
washed sugar liquor	66.9	7.48	65.12	0.04	0.02	1.78	0.9734
melt liquor	65.2	7.35	64.93	0.05	0.08	0.57	0.9913

Table 3. Analysis of refinery syrups

Sample	Brix	pH	%Sucrose	%Fructose	%Glucose	Brix - sucrose	Sucrose / Brix
set A							
filtr'd liquor	63.2	9.55	61.48	-	-	1.72	0.9728
light first liquor off char	62.2	8.50	61.20	-	-	1.00	0.9839
heavy first liquor	65.0	8.25	62.28	-	-	2.72	0.9581
first syrup	61.5	8.20	57.98	-	-	3.52	0.9428
Set B							
filtr'd liquor	62.8	8.65	61.94	-	-	0.86	0.9863
light first liquor off char	63.3	8.55	62.77	-	-	0.53	0.9916
heavy first liquor	65.8	8.40	63.22	-	-	2.58	0.9608
first syrup	65.7	8.40	64.02	-	-	1.68	0.9744
set C							
filtr'd liquor	63.7	9.30	63.23	-	-	0.47	0.9926
light first liquor off char	63.0	8.00	62.60	-	-	0.40	0.9937
heavy first liquor	67.3	7.80	65.36	-	-	1.94	0.9712
first syrup	60.6	7.55	58.71	0.05	0.07	1.89	0.9688

Results on analysis of refinery samples are shown in tables 2 and 3 for three sets of composite samples, A, B and C. Results on glucose and fructose are shown only in table 2, for samples up to the press-filter station. Analysis of glucose and fructose by the method in use in this study has a limit of detection of 0.01% of either sugar, and samples after filtration had less than this amount of invert sugars. Theoretically, it should be possible to use a higher concentration of sample than the dilution used here, but at high sucrose concentrations the viscosity of the sample apparently interferes with the analysis, and poor results are obtained. So, where no figures are given for glucose or fructose, it may be assumed that their concentrations were less than 0.01%.

The results given are in % on samples are received, not on a true solids basis. Refractometer Brix readings are given as a basis for comparison on an "apparent purity" basis. The heavy liquors after evaporation had been diluted at the time of refinery sampling to prevent crystallization, and so the concentrating of light to heavy No. 1 liquor is not reflected in these analyses. It is planned to put these analyses on a true solids comparison basis, either by freeze-drying the sample to determine total solids, or by determining the water in the samples, probably by the Karl Fischer method.

Results on fructose and glucose apply only to the early stages of sampling. It was expected that invert would be formed during defecation, but it is apparently destroyed there also, since no significant invert levels were observed in the press-filtered liquor. The small increases in apparent purity (sucrose/Brix) of less than 1% indicate that some sucrose has been lost, since more than 1% of non-sucrose solids would be removed in carbonatation. Analysis of the remaining samples for the affination and defecation stages will show more detail in the progress of invert formation and removal.

It is surprising that in only one case, set C, appreciable invert is observed in the first syrup. The pH in this syrup is rather lower than those of sets A and B.

Glucose and fructose analyses on raw sugars show the expected inbalance in the concentrations of the two monosaccharides. Six raw sugars, in all, were analyzed, and of these, four had a G/F ratio of less than 1, and two, a G/F ratio of more than 1. Both refineries sampled blend some remelt liquor with their melter liquor: the melt liquor analyzed here is the blended mixture. In one case, set C, it appears that the added remelt contained a high level of invert, which increased the melt liquor level above that of washed sugar liquor. This sort of recycling of impurities puts a double load on the clarification station. In set B, the apparent purity of the melt liquor is actually less than that of the washed sugar liquor, presumably because of the high level of non-sucrose solids in the added remelt.

The sucrose concentration can be examined at this point only from the point of view of apparent purity. When a viable analysis for total solids has been made, these results can be interpreted more meaningfully. At the present level of investigation, the fact that analyses for sucrose alone, unaffected by invert or other sugars, can be made on refinery liquors, means that sucrose levels, and sucrose loss, can be observed with an accuracy heretofore unavailable. A problem with these analyses, however, is that only total losses of

sucrose are shown: there is no differentiation between chemical and physical losses; physical losses, e.g. these from adsorption (6), have been examined quite thoroughly, and their sources can be identified on an objective basis.

The expected increase in apparent purity is observed across bone char treatment. There is, however, an unexpected and very large drop, when light first liquor off char is condensed to a higher Brix. Since the heavy liquors were diluted upon sampling, their actual Brix of 70 to 72 is not shown here. Although it is possible that dissolved scale in the evaporators caused some increase in the non-sucrose solids, and that the heating caused some loss of sucrose through chemical decomposition, it is extremely unlikely that such a large drop would occur so regularly, and the authors ascribe this difference to some error in sampling or sample preparation.

This study has pointed out some areas of particular interest to be investigated from the point of view of sucrose loss: defecation and crystallization are two. But the work so far has really emphasized the complexity of this problem. With this new tool, HPLC, that can be used for analysis on actual process samples without changing them chemically, further work is planned in which sucrose losses will be observed in different refinery processes; the various sorts of defecation and decolorization processes will be observed, analyzed and compared. It is planned that other aspects of HPLC analysis, for carboxylic acids and other organics and high molecular weight compounds, will be utilized to observe the colorants and other compounds that are eventual products of sucrose degradation and loss.

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DISCUSSION

R. K. Sinha: (Calgon): You indicate that you were studying the carbonatation process. Was any attempt made to look at the pH levels or how constant the pH was for the four sets of data?

M. A. Clarke: Yes. The pH levels are given in the tables included in the paper.

R. K. Sinha: When you go to the phosphatation process or to the carbon filtered process do you see that glucose/fructose levels increase?

M. A. Clarke: I think that we will see changes in reducing sugars with other decolorization processes. We are trying to determine a way to analyze much smaller amounts of invert in large amounts of sucrose. Theoretically, a more concentrated solution instead of the current dilute sample should show up smaller concentrations of invert but there are problems: If the sample is very viscous, as it would have to be to increase the invert concentrations, something, we think it is viscosity, stops the column from separating properly, so we don't get a decent analysis. We hope, however, to work out a method to read lower concentrations of invert.

R. K. Sinha: Are you planning ultimately to look into what is the impact on sugar recovery as a result of these chemical changes that take place in the process?

M. A. Clarke: Yes, over the unit processes. From our point of view, we can't look at the mass balance on the whole refinery because we don't know how much recycling goes on--and there would be a terrific amount of sampling involved. Of course the people we are getting the samples from can use the figures to calculate their own mass balances. The point of this study is to see what kind of sucrose losses you get at various processing stages. We know that there are sucrose losses in the refinery that haven't been identified yet. We plan to use this approach to pinpoint the places that have not been identified before. We hope to find some characteristic compounds that form on decomposition, so that we can say: Every time these compounds show up, there has been some sucrose loss.

R. Cormier: (Redpath): What type of integrator did you use in your work?

M. A. Clarke: There is no integrator. We are using peak height. The accuracy could probably be improved with an integrator, but we have not been able to obtain one. Our method of bracketing samples with standards gives better accuracy and precision than most of the work in the literature.

R. Cormier: From your experience, would you have any suggestion to make about the sampling procedure to be used?

M. A. Clarke: Those who are analyzing the samples should be told absolutely everything that has been done to them from the time that they were extracted

from process. If the analyst knows that has been done to a sample, then if something funny shows up, he will have an idea why.

R. Cormier: An interesting aspect of the HPLC's method of analysis is that it is easily amenable to automatization. For instance, we, at Redpath use that feature where, after loading the automatic injector in the late afternoon, the work is automatically done for us overnight.

M. A. Clarke: Yes, the procedure is easily automated. A single analysis for fructose, glucose and sucrose takes from 10 to 15 minutes.

J. F. Dowling: (Refined Syrups): In your analyses, you determine sucrose and then you divide it by a brix number. The brix on a char liquor is about 65 and the sucrose is like 62. No invert appears but there is about 3% difference between brix and sucrose. It would seem that if we are going to measure the sucrose, we have to get maybe a Karl Fischer analysis for water, or a total weight of solids, so we can follow those sucrose values properly. If we are going to work with the brix, I think we are in trouble.

M. A. Clarke: We are only using brix as a temporary measure for this report to get some sort of values for purity. In the paper we mention that we know that it is not right to work with brix, but because of different concentrations in the refinery we need something that we could use at all stages until we can get a water analysis or a true solids analysis. The work done by Huletts, in Ms. Morel du Boil's paper, using the chloride measurement to follow solids concentration is very useful for samples in and out of the pan because the chloride is not being removed or increased overall. What goes into the pan in the first liquor comes out either in the sugar or the first syrup. So you can use the chloride as a measure of the total quantity of solids there. But in char filtration or defecation, this method won't work. So what we are going to do--it is just a matter of time and equipment--is to get a true total solids directly or by a water analysis, and see how much of everything is there, and how much of that is sucrose. I think that the stage we are at right now is a step forward, however--we can see how much sucrose is there, not how much polarization.

R. Moroz (Revere): Is there any value in changing the acetonitrile concentration to detect the products of invert sugar destruction during carbonatation? You are using an 83/17 ratio of acetonitrile to water, which resolves sucrose, glucose, and fructose. If you change that ratio would the pattern of resolution change?

M. A. Clarke: We have tried different ratios because the amount of water determines the speed at which the compounds come out. But we have not seen any effect on the glucose and fructose levels.

R. Moroz: Did other impurities come out at the different ratios?

M. A. Clarke: I see what you mean: if there were more water, more impurities would wash out. No, we did not find that.

SUGAR CROPS FOR FUEL USE

by Edward S. Lipinsky

Batelle Columbus Division

INTRODUCTION

In its search for energy independence, the United States has turned its attention to biomass as a renewable source for fuels for transportation, heating, and/or electricity. The leading contenders for production of liquid motor fuels are trees and carbohydrate crops. The trees would be converted to methanol by thermochemical means (Reed, 1978); the carbohydrate crops would be converted to ethanol by microbiological means (Lipinsky, 1978).

Cane refiners purchase raw sugar and purify it for use in food applications. Numerous papers and government reports have been prepared by Battelle and others on other aspects of this fuels from sugar crops system. This paper is designed to provide cane refiners with relevant information.

SUGAR CROP SYSTEMS

As shown in Figure 1, a fuel-oriented sugar crop system can employ either the microbiological or the fermentation approach to fuel production. If the microbiological route is selected, ethanol is the usual target. If the thermochemical route is employed, methanol is the usual target. These target fuel chemicals are intended for liquid motor fuel use because they can obtain credit not only for their energy content but also for their octane improvement in this application.

The selection of the sugar crop or crops for use in a fuel from sugar crop system in the United States depends primarily on the following factors:

(1) Availability of sufficient sugar crop biomass to make a significant quantity of fuel

(2) Sufficiently low cost of production to render this source competitive in the long run

(3) An attractive energy balance so that more fossil fuel is not consumed in producing the crop than is manufactured from the crop.

Other factors, such as the quality of land required and the environmental capacity of intensive sugar crop agriculture, also are important but the three factors cited above are the most crucial.

In its systems studies for U. S. Department of Energy, Batelle has explored the possible use of sugar cane, sugar beets, and sweet sorghum as

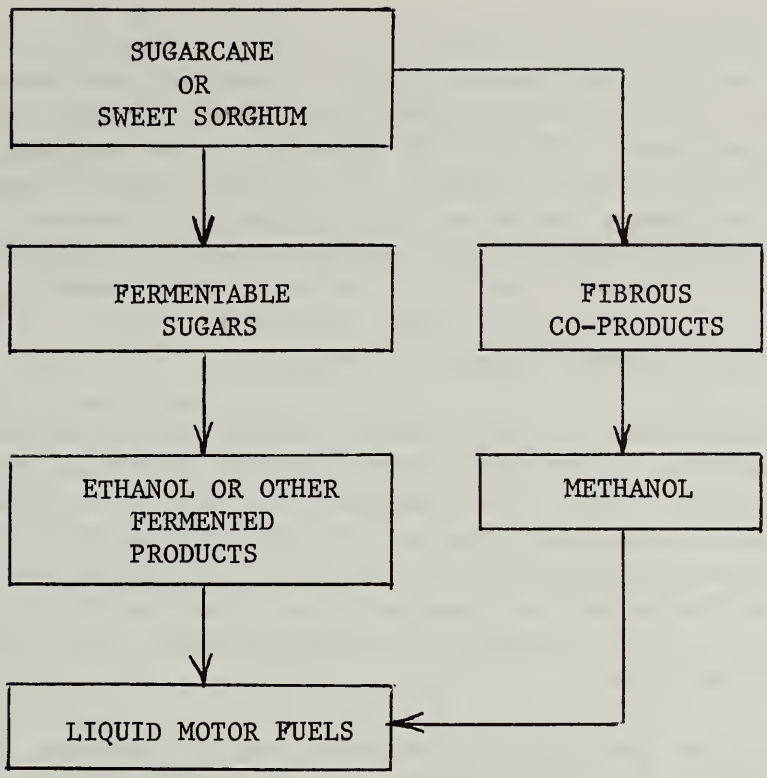

FIGURE 1
SUGAR CROP SYSTEM

sources of liquid motor fuels (Lipinsky, et al, 1976 and 1977). As you might expect, no sugar crop proved to be ideal for the United States. Sugar beets appear to be high in cost and to have a poor energy balance. With some agronomic improvements that have been suggested and recently verified, sugarcane can be quite economical and have a very favorable energy balance but can be the source of only a limited quantity of liquid motor fuel. Sweet sorghum has an attractively low cost, favorable energy balance, and a high potential availability. However, it is perishable and has a high seasonality. Thus, none of the sugar crops are ideal at the present stage of technology.

FUEL USE IMPACTS

From the cane refiners viewpoint, the major impacts of using sugar crops for fuels arise from the following considerations:

(1) The fuel market is much larger than the food market

(2) Fermentation consumes sugar juice that might be used for food

(3) Production of fuels by fermentation requires cheap juice which might be quite crude in composition.

These considerations represent common sense but they may have great practical implications.

Relative Market Size

The liquid motor fuel market in the United States exceeds 100 billion gallons per year. The United States consumption of sugar is approximately 10 million tons per year. If all of this crop were converted to gasoline-like liquid motor fuels, only 1.6% of the United States demand would be satisfied. Another way of expressing the disparity between the size of the fuel market and the food market of sugars is that it would require 650 million tons of raw sugar to supply the total United States gasoline demand. The implementation of any fuel sugar crop program is likely to involve a scale that is large by the sugar industry standards.

To obtain quantities of fermentable sugars that are of significance in the motor fuel market, it probably would be necessary to commercialize sweet sorghum because this is the only crop that we have been able to find that combines sufficiently high yields with sufficiently broad geographic range. The second major implication is that both sweet sorghum and sugarcane row spacings would be decreased to increase the yield per acre. The need to maximize production and to extend processing seasons may lead also to harvesting of frozen cane.

The vast size of the fuel market may lead to the use of new sugarcane and/or sweet sorghum varieties that are high in fiber and relatively low in sugar content. These high biomass varieties might be excellent for methanol production by thermochemical means, with raw sugar as a by-product. The extent to which this strategy would be permitted would depend on the relative value of methanol as a liquid fuel (or industrial chemical) and sucrose as a food product.

Crude, Cheap Juice

The manufacture of ethanol or other energy-rich fermentation products from sugar crop juice makes use of the fermentability of simple sugars. The major goals of cane refiners which include high sucrose concentrations (versus invert sugars), low color body concentrations, etc. are of no consequence to the ethanol manufacturer. The presence of starch or dextran which has such a deleterious effect on crystallization is of only minor importance to the ethanol manufacturer. It is deleterious to the ethanol manufacturer in that starch and dextran ties up glucose that might otherwise be converted to ethanol.

Sugarcane or sweet sorghum that has been damaged by insects or frost also are quite acceptable for use in the production of ethanol. Even dirt and fibers are quite acceptable, as is chlorophyll from the leaves of trees. Therefore, when the ethanol manufacturer says he is willing to settle for a very crude juice, he really means it.

Although the ethanol manufacturer is very accommodating with regard to a wide range of juice composition, he is extremely demanding with respect to the price that he must pay for fermentable sugars.

Depending on the relative quantities of sucrose and invert sugars, 12.5 to 14 lbs of fermentable sugars are required to manufacture one gallon of ethanol. When ethanol is used to replace gasoline, its value is approximately $0.60 per lb, before any subsidies or incentives are added. If fermentable sugars are available for $0.05 per lb, the economic price level has been exceeded even before any allowance is made for processing or profit. As the price of petroleum rises or if subsidies and incentives are provided, the economic constraints on the cost of sugar crop juice will be relaxed somewhat.

Our technical and economic studies indicate that radical changes in sugar crop technology must be undertaken to attain low sugar crop juice cost. It goes without saying that process steam and electricity will be produced from those parts of the sugar crop plant that are not needed either for soil conservation or for fermentable sugar production. This energy self sufficiency and opportunity to sell some electricity into the national grid will contribute to energy self sufficiency. However, the steps to attain low juice cost involve primarily isolation and sale of rind fiber for use in the manufacture of wood substitutes and pulp and paper products. These fiber coproducts can share the sugar stalk crop production costs so that less cost needs to be allocated to the juice. Ultimately, special varieties may be bred to obtain the optimum balance of high quality fiber and fermentable juice.

The need for cheap sugar crop juice and high quality rind fiber evokes the following major innovations:

(1) Sweet Sorghum

(2) The Tilby Cane Separator

Sweet sorghum is potentially a lower cost source of fermentable sugar because it will grow on any land that is suitable for corn grain. It can be planted as a simple seed, unlike sugarcane that requires seed pieces. Our initial calculations (Tables 1 and 2) indicate that this crop might provide better returns than corn in the Midwest. Used in rotation with corn and soybeans, sweet sorghum might improve the returns from all of these crops. The Tilby Process which is described in the next section of this paper provides a means to obtain salable rind fiber, while simplifying the procedure by which fermentable juice is obtained.

Table 1. Theoretical Costs of Close-Spaced Sweet Sorghum Production

Costs	$/Acre Southern U. S.	$/Acre Midwest U. S.
Preharvest variable	$109	$ 69
Harvest Variable (a)	158	136
Machinery Ownership and Miscellaneous	75	81
Land	87	109
Total	$429	$395

Source: T. A. McClure and A. Scantland, 1978

(a) Harvesting with modified sugarcane harvester

Table 2. Comparison of Costs and Returns of Corn, Soybean, and Sweet Sorghum Production in the Midwest

	$/Acre Corn	$/Acre Soybeans	$/Acre Sweet Sorghum
Returns (a)	$215	$208	$435
Costs of Production	203	153	395
Net Returns	12	55	40

Source: U.S.D.A., "Costs of Producing Selected Crops in the U.S.", and Battelle estimates in McClure and Scantland, 1978

(a) Corn = 100 bu/a at $2.15/bu; Soybeans = 32 bu/a at $6.50/bu; Sweet Sorghum = 8.8 dry tons/a at $49.43/ton (fermentable sugars at $80/ton; rind fiber at $40/ton; pith fiber at $30/ton; and silage at $40/ton).

Tilby Cane Separator Process

As shown in Figure 2, sugar stalk crops (i.e., sugar cane and sweet sorghum) consist of distinct zones when examined in cross section. The core of the stalk consists of pith cells that are then-walled and which contain over 90 percent of the sucrose. In addition to the pith cells, there are fibrovascular bundles. Surrounding this central zone is the rind which gives strength to the plant. The outermost zone is the epidermis which is waxy and prevents evaporation of water from the juicy stalk.

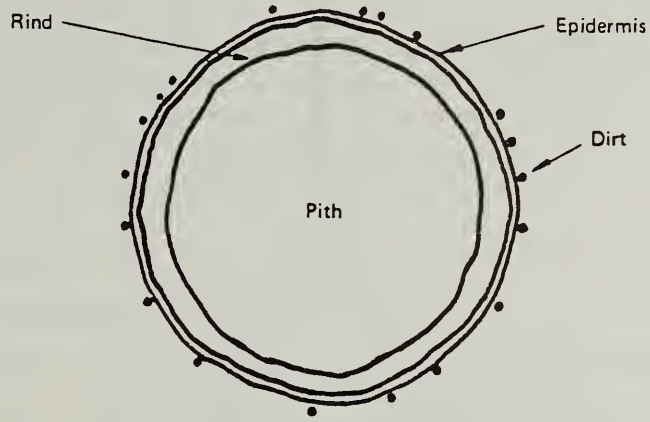

Figure 2
Cross section of sugar stalk

In conventional sugarcane milling operations, the epidermis, rind, and pith are mixed with highly deleterious results. Fibers that would be desirable for the manufacture of pulp and paper are mixed with pith cells that consume excessive amounts of pulping chemicals. Color bodies that complicate the production of white refined sugar and waxes that need to be removed by clarification are brought into contact with the sugar juice. The sugar technologist mixes constituents that Nature had kept separate and pays a heavy penalty in yield, energy, and money to reseparate the constituents.

The Tilby Cane Separator Process maintains the integrity of the stalk cross section. It was invented in the early 1960's and has been improved mechanically to a considerable extent in the last few years (Atchison, 1977 and Andersen, 1978). The basic patents are held by the Canadian Patents and Development Limited (e.g., Tilby, 1976), with Intercane Systems Incorporated and Hawker Siddeley as the principal licensees. The principle of this new process is to maintain the separation of the zones by scraping away the pith cells from the interior of a split billet and scraping epidermis cells from the exterior of the billet (Figure 3). The process represents quite a feat of material handling in that the billets are split and scraped one at a time at high speed. Although the process is extremely simple in principle, the stalk must be well detrashed and cleaned. Investigations of the process economics and the value of the multiple products that result from the Tilby Separator are underway at this time.

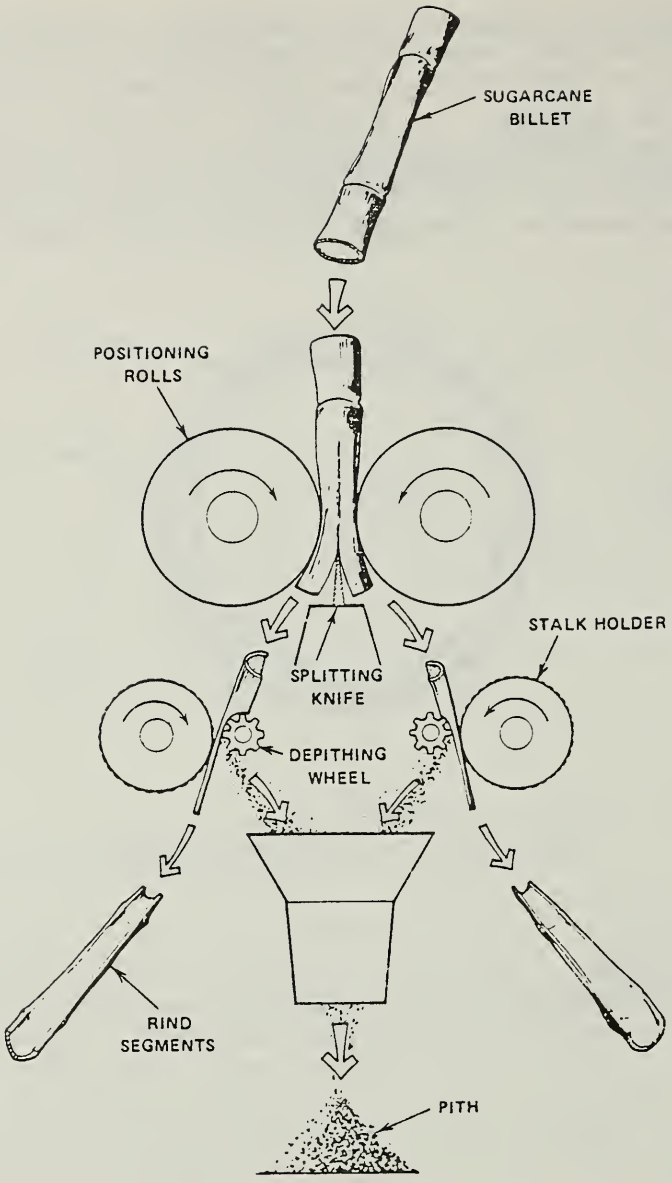

Figure 3
The Tilby cane separator process

Among the major implications of the Tilby Process are the following:

(1) Rind fiber is produced in strands that appear to accept adhesives well because the protective wax is absent.

(2) The rind fiber accepts pulping chemicals well because wax is absent and residual sugars that consume pulping chemicals can be washed away readily.

(3) The dirt-free pith contains over 90 percent of the fermentable sugars and can be extracted readily.

(4) The desugared pith appears to be an excellent cellulosic source of glucose or can be used for cattle feed.

Thus, a major attraction of the Tilby Process is the potential for sale of products other than sugar from the sugarcane stalk or sweet sorghum stalk. Co-product sales would allow reassignment of a lower cost to the sugar crop juice for processing into fuel. This opportunity for sale of coproducts also could lead to a reallocation of costs so that the sugar crop grower and raw sugar processor could reduce the selling price of raw sugar while making more profit.

Sweet Sorghum

Sorghum bicolor (L.) Moench, which is commonly called sweet sorghum, stores sugar (principally sucrose, glucose, and fructose) in its stalk in a manner similar to that of sugarcane. Some carbohydrate is stored as starch in a dwarf grain head. Thus, this crop has some grain sorghum and some sugarcane structures. Other important attributes are:

(1) Sweet sorghum could grow almost anywhere that corn or soybeans will grow

(2) Sweet sorghum is a crop with a very short processing season

(3) Sweet sorghum stores its carbohydrates primarily as simple sugars that are highly perishable

(4) Sweet sorghum frequently will out-yield corn or grain sorghum by a wide margin.

Because of these attributes, sweet sorghum initially might be used as a means to extend the season for a sugar crop that has a longer processing season.

Sweet sorghum can be planted in sugarcane areas so that this crop can be processed prior to the conventional sugarcane processing season. This type of incremental production could have very desirable impact on production costs because the facility and business organization are already in place. The added quantities of ethanol that could be made in this way are not of great importance from a national energy policy viewpoint. However, this low cost source of sugar could be of great value to raw sugar users and refiners.

Sugar beet producers have been hard pressed to compete during the mid 1970's. A major sugar beet problem is the need to rotate sugar beets with other crops to prevent excessive losses due to attacks of nematodes and other pests. Another problem has been that at least part of each sugar beets crop must be harvested prior to optimum maturity so that the processing facilities can be operated for an optimal percentage of the year. The production of sweet sorghum as a rotation crop with sugar beet might improve beet's position somewhat.

In some areas, sweet sorghum varieties and planting dates might be selected such that the sweet sorghum crop could be harvested and used instead of relatively immature sugar beet for the production of sugar early in the season. Sweet sorghum might be sufficiently resistant to mematodes and other sugar pests to be a direct rotation crop with sugar beets. Thus, the beet framer could remain a sugar farmer. These concepts would require that the beet processing facility add a Tilby device or other means to extract sweet sorghum juice.

These table sugar production concepts are offshoots of ideas currently under investigation for integrating sweet sorghum with other sugar crops to maximize the fermentation season to reduce the cost of fuel-grade ethanol.

THERMOCHEMICAL OPTIONS

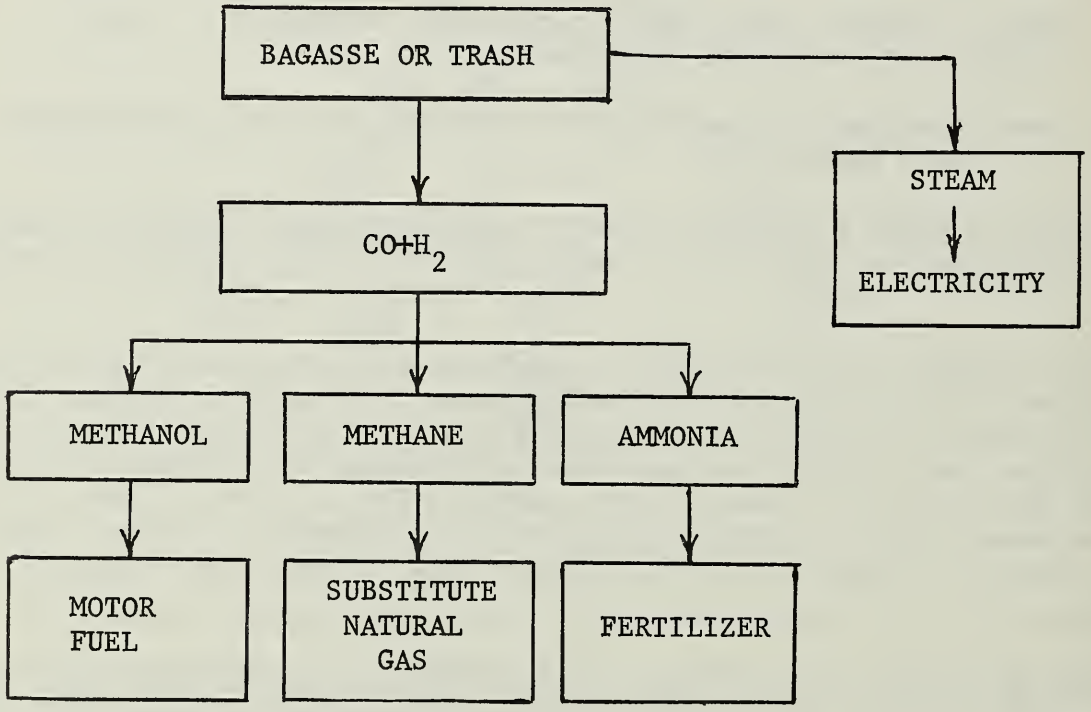

FIGURE 4

ROUTES FOR THERMAL CHEMICAL PROCESSING

THERMOCHEMICAL OPTIONS

Because sugars are so readily fermentable, sugar crops are thought of primarily as a means to manufacture fuels by microbiological processes. However, bagasse and/or trash could be converted into fuel by thermochemical means. As shown in Figure 4, there are two major routes to thermochemical processing. In the first, the material is simply burned and used to produce steam and electricity. This approach is not glamorous but energy self sufficiency is likely to be more highly valued in the future than in the past. A significant alternative against which energy self sufficiency should be measured is the production of a mixture of carbon monoxide and hydrogen known as "synthesis gas". This synthesis gas can be employed to manufacture methanol, methane, or ammonia. Methanol can be blended with gasoline in a manner similar to ethanol. Methane can substitute for fossil natural gas in home heating or cooking. Ammonia can be used as a fertilizer, with savings of natural gas now employed in making this agricultural chemical.

The major advantage of thermochemical processing is that the fuel production does not compete with the food production as it does when sugars are fermented. The major disadvantage is the relatively small scale that is implied when the fibrous coproducts associated with the present United States sugar consumption are employed to make a contribution to the solution of United States energy crisis. Also, when the gas is diverted to thermochemical production of fuels, there is still a need for fuels from production of raw sugar. If that need must be supplied by fossil fuel, relatively little may have been gained.

CONCLUSIONS

Sugar stalk crop production may skyrocket to satisfy a demand for automotive fuel. Such an increase in production is likely to arise primarily because of the development of sweet sorghum as a sugar stalk crop and by use of close-spaced sugar stalk crops as a means of raising yields.

The sugar crop juice that results from a fuel-oriented market demand may not be fit for raw sugar production because there is no incentive to work with low invert sugar varieties, for example. On the other hand, the development of the Tilby Cane Separator Process makes possible the generation of highly pure sugar crop juice, even if the original development is directed toward fuel production.

Provided that disadvantages with respect to economies of scale could be overcome, thermochemical conversion of nonsugar parts of sugar crops plants might yield salable fuels as coproducts of raw sugar production.

Producers and refiners of sucrose need to develop new technology to remain competitive. It is ironic that the energy crisis is providing impetus for the development of resources and processes that could be used to reduce the cost of raw sugar.

The cane refiner is not likely to find that potential raw sugar would be bid away by a high-paying fuels market. On the contrary, the fuels market is likely to be extremely price conscious. It may permit economies of scale and coproduct sales that will reduce the cost of raw sugar to cane refiners. It is possible that new processes could provide raw sugar of higher quality to the cane refiners.

Acknowledgements

The author acknowledges financial support from the Department of Energy under contract No. W7042 ENG92. The author also gratefully acknowledges the intensive efforts and suggestions of T. A. McClure and S. Kresovich at Battelle.

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M. C. Bennett (Tate & Lyle): Mr. Lipinsky has covered an absolutely vast subject. I would like to make the point that what he is speaking about, power alcohol programs, are actually in existence in the world today, for example in Brazil. The introductions of such programs are not dependent on the development of new technology because the existing technology is quite adequate. Specifically, a modern mill tandum will crush anything it is given, so why cloud the issue with new untried technology? What is far more concern is the energy balance. Will you actually gain energy or not?

In Brazil they have embarked on a program to substitute 20% of their gasoline by 1980. In the late 1980's they want to substitute 50%, and by the 1990's the whole lot. Well you can work out how much sugarcane you would have to grow and work out what acreage of land you would need to plant that cane. And even Brazil just doesn't have that amount of sugarcane land available, so as Mr. Lipinsky said, you have to look around for other sources of fermentables. He has been talking about sweet sorghum, but in Brazil they have been looking at cassava, a root crop. But if you study the energy balance in producing alcohol from cassava you will find that there isn't really much of a net energy gain. It takes a lot of energy to plant the crop, cultivate it, bring it into the factory, make the alcohol, and truck it to the city, and furthermore, you have to make the fertilizers, so that you really end up almost on break even. So if you are going into such a program for an energy gain, you are not actually achieving your objective.

So, I would like to ask what sort of energy gains can be achieved by these programs? This is regardless of the capital and operating costs, because no one knows what the price of oil will be by 1990.

E. S. Lipinsky: Yes, we have turned out several thick reports on this, and it involves really a matter of energy accounting. It turns out to be a real jungle compared to ordinary accounting. Our numbers agree fairly well with a recent publication by Golbemberg and his associates that came out in Science magazine.[1/]

But both his estimates and ours are much more pessimistic than a number of others. We find that somewhere between 1.2 to 1.4 times as much energy is produced as energy is consumed. When you first grow sugarcane you are way ahead of the game. You have made seven units of energy for every one put in. But it is all down hill from there. You have to squeeze, ferment, distill, and dry the stillage. However, you end up still a little bit ahead. We have had two teams making these calculations. The two teams have not fully agreed on all items but we do have a small positive energy balance, although only for sugarcane and sweet sorghum. As soon as we go to any of the starch crops like corn, and I am sure cassava would be in the same position, these several other steps start to really hurt. We feel that the conventional way

1/ Goldemberg, et al, Energy balance for ethyl alcohol production from crops. Science 201, 903-906, Sept. 8, 1978.

of looking at the energy balance is wrong. Let's just take the distillation situation. The calculations that have been done by us and by everyone else have used conventional distillation. The new pressure distillation and extractive distillation methods by Katzen [2/] cut this energy consumption by about 30%. Our energy calculations on going from 95% ethanol to 100% ethanol use conventional azeotropic techniques. But there are solvent extraction methods that would take water out that wouldn't take any extra energy.

The evaporative drying to get the stillage to a solid form for cattle feed requires about 30% of the energy for the whole operation. But we could do an anaerobic digestion instead and get methane gas with much less energy consumption.

So although the technology to make motor fuel alcohol does exist, we think that almost none of it is worthwhile for the new era that we are trying to enter now.

That is why we think we need a new sugarcane processing system, a new fermentation system, a replacement for distillation, etc.

D. E. Tippens (Amstar): Are you doing any work on the conversion of the cellular mass enzymatically to dextrose and then further conversion to alcohol?

E. S. Lipinsky: Our laboratory is not. There are many groups working on that problem. Berkeley, MIT, U. of Penn., General Electric, Rutgers, and Purdue are examples. There have been some breakthroughs in that area which we have been evaluating. There is a family of processes called the Purdue process. This essentially makes cellulose amorphous; it then behaves a great deal like starch and is much easier to convert enzymatically to dextrose. And it allows one to do this in a much more concentrated solution, than the Natick or Berkeley processes.

Then there is a Canadian process called the Iotech process which is a variation on the old Masonite or Puffed Wheat process. This process extracts the lignin from the cellulosic material and results in cellulose chains that are quite far apart. This is an effect that is very similar to what you get with the Purdue process. But when you examine the Iotech Product by X-ray diffraction you find that the cellulose is still crystalline, although it behaves as if it were starch. We feel that with these improvements in the cellulose-to-dextrose route, this area will be a very strong contender with the sugar crops in the race for alcohol or other fermented fuels.

B. S. Garrett (Rohm & Haas): In Brazil one of the problems you mentioned has been waste disposal of the stillage, and there are going to be massive quantities of that. Some of the material is now being used as fertilizer. Do you have any comment on what direction this might take in such a massive program?

2/ Katzen, R., Diebold, V, Distillation and purification of a mixture containing crude alcohol, USP 2545508 (1976)

E. S. Lipinsky: That is a question that a lot of people are worried about right now. One technique that has been recommended by Alfa-Laval is used on Kraft pulp mill waste. In this process the waste is burned and there is enough organic content in stillage to support combustion and evaporate the water. What one isolates from that is a solid material that is high in potash which can be used for fertilizer. This seems to be a distinct improvement over the Brazilian system which puts the stillage in tank wagons and then sprays it on the fields. They will probably not use that much longer.

There is also the evaporation to dryness to obtain sugar distillers dried solubles. The most knowledgeable people in this area are the South Africans who work for NCP. For many years they have been making a molasses distillers dried solubles and blending that with other animal feed imgredients and successfully marketing that product. It has about 10% protein, and 30 to 40% salts which can cause problems with diarrhea in the animals unless it is blended properly. However, it takes a lot of energy to evaporate the stillage to dryness.

C. C. Chou (Amstar): Whether there is a net gain on an energy project, such as energy farming, and gasohol, etc., it depends upon the boundary you draw to make the calculation, and how you draw the boundary depends upon which camp you are in. So what we need is an unbiased third party to make the judgment.

E. S. Lipinsky: That is one of the real problems in systems analysis, where do you draw the boundary in energy balances. We look at it from the point of view of the amount of fossil fuel consumed in the actual production. For instance, in growing sugarcane we would count all the tractor fuel, all the fertilizer, but we would not count the energy that went into making the steel that went into the tractor. And we would not count, as the Brazilians count, the food calories that went into the laborers that harvest the cane. So our boundaries include the fossil fuels used in the production and also in the conversion including the squeezing, etc. We keep score, in terms of natural gas, diesel fuel, electricity, etc., and we think it is important to know when we are using diesel fuel vs. when we are using electricity, because we can get electricity from domestically produced coal whereas we may have a hard time getting diesel fuel from domestically produced oil in the future. We draw our boundary differently from say Pimentel at Cornell.

F. G. Carpenter (CSRRP): You drew your line around the tractor, but if you didn't use a tractor, you would have used people for the job so you should have included the people in too.

E. S. Lipinsky: We drew our line where we chose to. For our country we did it that way. In Brazil, they drew it around the people because the alternative is to have the people unemployed.

MINIMUM ENERGY FOR REFINING SUGAR

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ABSTRACT

The energy required in various processes in sugar refining was evaluated on theoretical grounds. Evaporation of water is by far the largest energy use, with heating water and sugar second. All other energy requirements are far less. Good recovery practice can easily reuse 40% of the energy. Although some refiners come to within 20% of a practical energy goal, American refiners on the average, waste 73% of their energy.

INTRODUCTION

The rising cost of fuel has made saving energy the principal topic of discussion in virtually every industry. However, this is nothing new to the sugar industry. Sugar refining has always been an energy intensive process, and saving energy attracted the attention of sugar engineers long ago. To the everlasting credit of the sugar industry must go the greatest energy saver of all time: the multiple effect evaporator. This process is now used world wide by every industry that must evaporate water. It was invented by Norbert Rillieux (1) and first installed on Myrtle Grove plantation, a few miles below New Orleans in Louisiana. Every detail of multiple effect evaporation is contained in his patent and all the papers, articles, and books written about it since have only been restatements of his principles.

Another work, which is considered by many as a landmark publication, is Sir Oliver Lyle's book "The Efficient Use of Steam" which was published (2) 100 years after Rillieux's multiple effect evaporator, but still 30 years before the high price of fuel made the world energy conscious. Modern researchers on saving energy need only look to Sir Oliver's book because all the principles are there.

It is, however, instructive to evaluate some theoretical and practical minima in the use of energy in refining sugar to see just how low it might ever be possible to go. The results may be surprising.

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(1) Rillieux, Norbert, U.S. Pat. 4879 (1846).
(2) H. M. Stationery Office, London 1947.

PRESENT ENERGY USAGE

Energy usage in this report will always be expressed in:

BTU/lb

This means total energy from all sources converted to BTU and expressed per pound of raw sugar melted.

For those more familiar with the metric system:

divide by 1.8 to obtain cal/g

For those who insist on SI units:

multiply by 2326 to obtain J/kg

For those who think in terms of steam:

divide by 10 to obtain steam
used as a percent of melt

In Sept. 1976 the U.S. Energy Research and Development Administration (ERDA) (now the Department of Energy (DOE)) developed information (but did not publish it) that the energy usage in refining sugar was 5000 BTU/lb. This put sugar refining among the top users of energy among the food processing industries.

In 1978, at the S.I.T. energy symposium, Gerstenkorn (3) reported the results of a survey from 19 sugar refineries. The range of energy usage was from 650 to 3500 BTU/lb with the world average of 2000 BTU/lb and the U.S. average of 3000 BTU/lb. At that same meeting, Buckland (4) reported that the Thames Refinery in London uses 1000 BTU/lb. This then is the background of what is actually being used.

THERMODYNAMIC CONSIDERATIONS

Any theorist must first consider thermodynamics because these are three rules that can't be beat. Thermodynamics considers only the starting materials and final products, and not the route used. In sugar refining the starting raw sugar is crystalline sucrose of about 98% purity at room temperature.

The final product is crystalline sucrose of about 99.95% purity at room temperature. Thermodynamically speaking, the final product is in almost exactly the same state as the starting material.

Therefore the thermodynamic energy requirement approaches zero!

(3) Gerstenkorn, R. M., Energy Symposium, S.I.T. (1978) London.
(4) Buckland, W. G. N., Energy savings in cane sugar refineries, S.I.T. (1978) London.

How then is actual energy usage of the order of 1000 BTU/lb? It is simply that thermodynamics assumes that each step is carried out at equilibrium in a perfect way with no waste or losses. All heat that might be added is completely recovered as the product is cooled down. Any energy used to lift or accelerate is recovered upon lowering or deceleration. This would require enormous heat exchangers and other equipment, and the sugar would have to go through very slowly and easily. This is the direction that sugar refineries will have to go if energy costs go sky-high. If the price of fuel continues to increase, then it will be more economical to build larger refineries that use less energy.

ENERGY FOR PROCESS

At the opposite end of the scale from the thermodynamic refinery would be the energy intensive, minimum size, maximum throughput refinery.

This corresponds well with most actual refineries, especially those that are operating at above their design capacity. Consider now only the energy that is actually needed and used in the process, not that lost or wasted, or poor efficiency. Instead of going through the process step by step, generalizations will be made.

Lifting

Sugar Refineries are generally about 7 stories of 14 ft, or 100 ft high. All through the process the sugar is lifted many times. Assuming an average of 7.78 times to the top of the building this is 778 ft lb or 1 BTU/lb.

Pumping

Suppose the refinery operates at 66 Brix. Such a sugar solution has a density of 82.7 lb/cu ft. Further suppose that a 4 million pounds per day refinery uses 4-inch pipe to move all that melt around. The velocity in that pipe would be:

$$v = \frac{4000000 \text{ lb sug}}{\text{day}} \frac{\text{day}}{24 \text{ hr}} \frac{\text{soln}}{.66 \text{ sug}} \frac{\text{cu ft}}{82.7 \text{ lb soln}} \frac{\text{hr}}{3600 \text{ sec}} \frac{4}{\pi 4^2 \text{ sq in}} \frac{144 \text{ sq in}}{\text{sq ft}}$$

$$= 10 \text{ ft/sec.}$$

A different size refinery would use different size pipe but at approximately this same linear velocity, which is what counts in pressure loss through piping.

Using the concept of velocity head to estimate pressure loss, the velocity head for this velocity is:

$$v_h = \frac{v^2}{2g_c} = \frac{10^2 \text{ ft}^2/\text{sec}^2}{2 \times 32.2 \text{ ft/sec}^2} = 1.56 \text{ ft of fluid flowing}$$

(g_c = mass to force conversion)

Using the rule of thumb that a velocity head is lost for an equivalent pipe length of 40 diameters, for 4-in pipe the pressure drop is:

$$\Delta P = \frac{1.56 \text{ ft}}{40 \text{ pipe diam}} \frac{82.7 \text{ lb}}{\text{ft}^3} \frac{\text{ft}^2}{144 \text{ in}^2} \frac{\text{diam}}{4 \text{ in}} \frac{12 \text{ in}}{\text{ft}}$$

$$= 0.067 \text{ psi/ft pipe.}$$

Suppose that the refinery using 4-in pipe has an equivalent pipe length of 9000 ft. Then the whole pumping pressure loss through the whole refinery would be.

$$\Delta P = 9000 \text{ ft} \times 0.067 \text{ psi/ft}$$

$$= 600 \text{ psi.}$$

A smaller refinery would have smaller pipe - higher pressure loss per foot of pipe but less pipe and would amount to the same total pumping pressure loss.

This figure of 600 psi is the sum of all the pumping pressures of all the pumps on the main sugar liquor stream in the whole refinery, but does not include that part attributable to mere hydrostatic head which was considered earlier. The energy involved is pressure x volume.

$$\text{Pumping energy} = \frac{600 \text{ psi soln}}{.66 \text{ sug}} \frac{\text{ft}^3}{82.7 \text{ lb}} \frac{144 \text{ in}^2}{\text{ft}^2} \frac{\text{BTU}}{778 \text{ ft lb}}$$

$$= 2 \text{ BTU/lb}$$

Mixing

The minimum energy for adequate mixing is not easily evaluated, but its order of magnitude can be ascertained from analogy with pumping. The energy requirement does definitely depend upon the size of the inhomogeniety that must be mixed. In melting and crystallization this size unit is of the order of 1 mm which is the size of the crystal that is dissolving or growing.

In affination mixers the distance is a few hundred mm which is the distance that the syrup must be mixed into the dry sugar.

In all mixers some sort of pump-like device pushes some of the fluid over into another place in a manner similar to pumping. After this is repeated many times, say 100, the fluid is mixed.

So adequate mixing is like pumping about 100 times the size of the inhomogenicty. This is recognized as being equal or less than the pumping just evaluated so the energy for mixing can be considered as probably less than:

1 BTU/lb

Centrifuge

For good centrifuging, it is desirable to accelerate the sugar to about 1000 x G. This is accomplished in a 48-inch basket at 1200 RPM. The rotational energy under these conditions is:

$$E = \frac{w^2 I}{2g_c},$$

where w is the rotational velocity,

$$w = 2\pi N$$

and I is the moment of inertia

$$I = MR^2$$

The energy per pound of sugar is:

$$\frac{E}{M} = \frac{2^2\pi^2 N^2 R^2}{2g_c} = \frac{2\pi^2\ 1200^2\ \text{min}^2\ 24^2\ \text{in}^2\ \text{ft}^2\ \text{lb}_f\ \text{sec}^2\ \text{BTU}}{\text{min}^2\ 3600\ \text{sec}^2\ 144\ \text{in}^2\ 32.2\ \text{lb}_m\ \text{ft}\ 778\ \text{ft lb}}$$

$$= 1.26\ \text{BTU/lb}$$

All the sugar is centrifuged twice, so the rotational energy required is:

2.5 BTU/lb

And this only considers the sugar. The basket also turns and contains energy, but a regenerative braking system should recover that amount.

Char Regeneration

Bone char has a specific heat of about 0.21 BTU/lb °F. It is heated from 70°F to 970°F in the kilns. The sensible heat required is:

(970-70) x 0.21 = 189 BTU/lb char

This char contains about 20% water which must be heated to 212°F and evaporated.

Sensible heat = (212-70) x 1.0 x 0.2 = 28 BTU/lb char

Latent heat = 970 x 0.2 = 194 " "

Total heat for kilning bone char 411 " "

The char is washed before kilning with perhaps twice as much hot water as char. The heat in this water is:

(170-70) x 1.0 x 2 = 200 BTU/lb char

Total heat in char regeneration:

611 BTU/lb char

Assuming 10% char burned on melt, this heat per pound sugar is:

61 BTU/lb sug

Granular carbon systems use no wash water, have higher % water in carbon to kilns but regenerate only 1/10 as much carbon.

So the heat load is about:

5 BTU/lb sug

Heating Sugar

Assuming that the sugar and melter water start at 70°F and the whole plant operates at 170°F (77°C) and the operating brix is 66, the specific heat of sucrose is 0.30 and of 66 Bx soln. is 0.64.

Then the sensible heat in the sugar is:

(170-70) x .30 = 30 BTU/lb sug

Sensible heat in water:

(170-70) x 1.0 x .5 = 50 BTU/lb sug

Total heat to operating temp. 80 BTU/lb sug

In addition, if a phosphate clarifier is used, the solution is heated an added 40°F to 210°F.

Added heat for phosphate clarifier:

40 x .64/.66 = 40 BTU/lb sug

Evaporation

All the water added, which is 1/2 the weight of sugar, must be evaporated somewhere, in evaporators, pans, or driers.

The latent heat of this water is:

970 x .5 = 485 BTU/lb sug

Summary

The total energy required for process is summarized in table 1. This is the actual energy that is usefully used. No account has yet been taken of waste, loss, inefficiency, nor of recycling the sugar. Also no credit has been given for energy recovery.

Examination of table 1 shows distinctly what is already well known, that the big energy user is evaporating water. This is why Rillieux invented the multiple effect evaporator, and is the reason why future refineries will be built with more effects.

ENERGY SAVED BY RECOVERY

The only place where much of a dent can be made in energy requirements is in recovery and reuse of heat.

Table 1

Summary of Energy Required for Process:

	BTU/lb sug	percent
Lifting.	1	1
Pumping.	2	
Mixing.	1	
Centrifuging.	2.5	
Char Regeneration.	69	10
Heating Sugar.	120	18
Evaporation.	485	71
Total.	680	

Char Regeneration

It is quite reasonable to assume that most of the sensible heat in the bone char can be recovered and used for drying the char. Likewise at least half of the heat in the char sewer water could be saved by recovery. This would lower the bone char regeneration energy to 30 BTU/lb.

In a granular carbon system only the sensible heat could be collected but this would only reduce the heat load to about 4 BTU/lb.

Heat in Sugar

Only about half the sensible heat in the sugar could be easily recovered in the coolers. This would reduce the sensible heat to 65 BTU/lb.

Evaporation

An evaporation scheme that averaged out to double effect would be like dividing this heat by 1.9; for a triple effect, dividing 2.8. This heat load would then be:

Double	255 BTU/lb
Triple	173 BTU/lb

Summary

The overall effect of these recovery schemes are summarized in table 2. Most of the evaporation in a refinery is done in vacuum pans where making a double effect is difficult, let alone a triple effect. So the figures for a double effect are probably more realistic. Even so, lowering the energy requirements from 680 to 400 BTU/lb represents an easily recovered 40% of the energy.

Now it is conceded that many minor details have been omitted and likewise because of recirculation the sugar on the average probably makes nearly two statistical trips through the refinery, so far a more practical figure, those given in table 2 should be multiplied by 2.

Table 2

Energy Requirements when Using Recovery.

Energy Use	Phosphate Bone Char Double Effect	Gran Carb Triple Effect
Lifting.	1	1
Pumping.	2	2
Mixing.	1	1
Centrifuging.	2.5	2.5
Char Regeneration.	30	4
Heating Sugar.	105	65
Evaporation.	255	173
Total	400	250

Table 3

Effective Energy Usage.

	Energy Use BTU/lb	Waste, Loss, and Inefficiency Percent
American Average.	3000	73
World Average.	2000	60
Thames.	1000	20
"Theoretical"	800	

If all the difference between actual energy usage and this "theoretical" minimum is ascribed to waste, loss and inefficiency. The figures in table 3 are obtained.

CONCLUSIONS

A figure of 800 BTU/lb was developed, albeit somewhat tenuously and with many simplifying assumptions, for the minimum energy that might be used in the practical refining of sugar. As was expected, all real refineries use more than this amount with the Americans on the average wasting or losing 73% of their energy.

If there is any message in these calculations it is certainly to save in evaporation. This might be done by adding less water to the sugar, or running at higher Brix. It could also be accomplished by selling syrups. It can also be done by making more use of multiple effects. It also suggests that a fruitful field for basic research would be on ways of avoiding evaporation of water by either using some other solvent, or some other process than evaporation.

It is also clear from tables 1 and 2 that substantial savings can be made only in the heating processes in refining. All of the mechanical handling involves very much smaller amounts of energy.

These figures, however, are for energy that should be used. Very wasteful or inefficient processes should be improved wherever they occur.

When considering the primary fuel input to refining rather than energy used in process it should be remembered that electrical or mechanical energy comes at only 30% efficiency from the primary fuel and low level heat is an excess by-product. From this point of view all the mechanical figures should be multiplied by 3 to put them on the same basis as the heat figures. Even in this case they are still small compared to evaporating water.

DISCUSSION

A. M. Bartolo (Imperial): I enjoyed your calculations, and I realize that steam is primarily used in heating sugar and evaporation. You have converted some fuel into steam and have not taken into account boiler efficiencies. Or, stated another way, you assume that you have 100% boiler efficiency which is not possible and not realistic.

F. G. Carpenter: I agree with that, but this calculation is in terms of energy used in process, not that required to supply all the losses and inefficiencies. If the price of fuel is very high, more efficient boilers will be made.

A. M. Bartolo: When I was visiting the Thames Refinery, I asked some pointed questions of the power plant operator, and their actual use may be 20 to 30% higher than the figure you obtained from their publication 1/ which is apparently for their best operation. Also they have a very unusual operation. They don't have any startups or shutdowns and that accounts for a lot of energy usage.

J. E. Morton (Redpath): In commenting on present energy usage with some little inside knowledge, because I worked with Gerstenkorn on the survey, I believe the American Dept. of Energy figure of 5000 BTU/lb that you give is a little bit suspect. However, the American average and world average do have a degree of conformity. They came from 19 refineries who all attempted to answer the same questions, and in fact some 5 or 6 didn't quite answer them and they weren't included. Thames was not one of the 19 responding refineries and I don't think the 1000 BTU/lb you quote is comparable to the 3000 BTU/lb American average or the 2000 BTU/lb world average. I agree with what Bartolo is saying, that it is probably somewhat higher.

1/ Buckland, W. G. N., Energy savings in cane sugar refineries, S. I. T. (1978) London

F. G. Carpenter: Thank you for giving us some improved current use figures. However, I am not worried about the exact values. Those figures were intended to give a level to think in terms of, and to awaken a realization of the magnitude of the losses. Gerstenkorn had one refinery using 650 BTU/lb. which is below my "theoretical."

J. E. Morton: I believe that the refinery you are referring to produced liquid sugar only. They had no evaporation. There was another liquid sugar refinery also.

Whilst we might all disagree with your "Theoretical" value of 800 BTU/lb for some reason or other, I happen to believe that if we go into Sir Oliver Lyle's book 2/ deeply enough we would agree that what you have is not a bad figure, however you get to it.

F. G. Carpenter: Thank you very much. Perhaps the figure of 800 BTU/lb is what the Dept. of Energy should be thinking of instead of 5000 BTU/lb.

C. C. Chou (Amstar): You stated that the thermodynamic energy requirement approaches zero. I think what you mean is the energy difference between the two states - the raw sugar and the refined sugar. The energy requirement, of course, depends on the "path" taken. In any case, the energy difference between the two states does not approach zero as you claimed. Separation of minute impurities from sucrose is not a spontaneous process, and there is a large decrease in entropy. Therefore, a considerable amount of work (energy) is needed to achieve the process. The ΔH is definitely very far away from zero.

F. G. Carpenter: The fact that the impurities are minute indicates that the thermodynamic energy difference is also minute, at least in comparison to the energy actually used. The point that I wished to make was that the thermodynamic energy minimum was not being approached, even remotely.

G. H. Van Diermen (Copersucar): You quoted the Thames Refinery as using 1000 BTU/lb. I remember this figure very well. Twenty years ago when I started with Amstar (American Sugar at that time) I was given the job of steam energy conservation. Mind you, 20 years ago. At that time I had the figure of 1000 BTU/lb that the Thames refinery already had, and this was our target. We never got down that far, but now being in Brazil I found out that there, they are running at this figure, but they are using a different process for making sugar, the amorphous process. You call it here micro-crystalline sugar. This is also a very important point to look into -- The way to get to dry sugar. The amorphous method of making sugar requires much less energy. So far, we have not done much on energy conservation in Brazil, yet. But we are already at the 1000 BTU/lb figure right now.

2/ Lyle, Sir Oliver, Efficient use of steam, H. M. Stationery Office, 1947.

F. G. Carpenter: I would like to take one slight issue with you. Theoretically the same energy is required to evaporate the water and produce dry sugar no matter how you do it. Whether you use a conventional vacuum pan or the amorphous process the theoretical minimum energy is the same. The amorphous process may be much less wasteful of energy.

G. H. Van Diermen: Yes, but we do not have affination, centrifuges, and centrifugal wash water to deal with. We do not have remelt boiling and we do not produce molasses which helps quite a bit.

E. S. Lipinsky (Battelle): I thought that I should mention that a principal sugar-oriented goal of the so-called Tilby Process has been to use the juice that comes from that in an amorphous sugar process rather than in a straight refining process. One is able to get a higher concentration of sucrose in the initial juice. This leaves some sugar in the pith which could be used for cattle feed. The idea is to have less water to be evaporated and also get a light color. I have not seen any of this amorphous sugar made from the Tilby process, because we are still working on fermentation as our scope. But that would be one combination to look at.

F. G. Carpenter: The calculations that were presented in this paper were for the refining part of the whole sugar process. Starting from the plant juice, whether it be cane, beet, or sorghum, there is much more water to be evaporated. The farthest behind are the maple sugar people who start with 2 brix. After they have evaporated 7/8 of the water they are up to where everybody else starts. And after you have evaporated 3/4 of that water you are up to where the refiner starts. So the refiner has the easy end of the whole process. The cane and beet mills have to evaporate a lot of water and they always use multiple effects, 3,4,5. And they take good advantage of the multiple effect evaporator. This paper was only addressed to the refining part.

E. S. Lipinsky: Your suggestion of a nonaqueous recrystallization is a splendid one and I hope you follow up on that one.

F. G. Carpenter: Also we could consider the other route. Instead of non-aqueous, a non-evaporative route but using water. It might use freezing or solvation of some sort.

The ion-exchange people are all asleep, because they should have been quick to point out that there is no kilning or heating in the regeneration of ion exchangers. They may have other problems but we won't bring up these.

J. E. Morton: When are we going to educate the consumer to ask for 100 color unit sugar. That would also save a lot of energy.

MICROCRYSTALLINE SUGAR: PRODUCTION, CHARACTERISTICS AND APPLICATIONS

Chung Chi Chou and Charles Graham
Amstar Corporation, New York, New York

INTRODUCTION

The process of drying sugar via the "transformation" of a highly concentrated sugar syrup has been known for many years. The sugars produced in this manner are found to consist of aggregates of microcrystalline sugars with various physical and functional properties which offer considerable commercial opportunities.

In the early 1950's, Amstar Corporation initiated an R & D program to study the nature of the process and to develop an efficient and flexible process to manufacture microcrystalline specialty sugars for the food industry. This program resulted in a series of U. S. Patents and the installation of the World's first highly automated continuous commercial process in the early 1960's. Since then two more installations have been added to the production line.

Our highly developed process technology, accumulated over two decades of manufacturing experience and continued R & D programming, enables us to tailor-make various products to meet market needs via feed material formulations and process control. Currently, Amstar markets four specialty sugars produced from the "transformation" process: Di-Pac®, Amerfond®, Bakerfond™ and Brownulated® Sugar.

THEORY

A process operation for tailor-made products requires proper control of the rate of nucleation, crystallization and thermal balance during the "phases" change stage.

The rate of nucleation in a perfectly pure sugar solution can be approximated by the general equation of reaction Kinetics: (1)

(1) Nielsen, A. E. Kinetics of Precipitation, Pergamon Press, Oxford (1964).

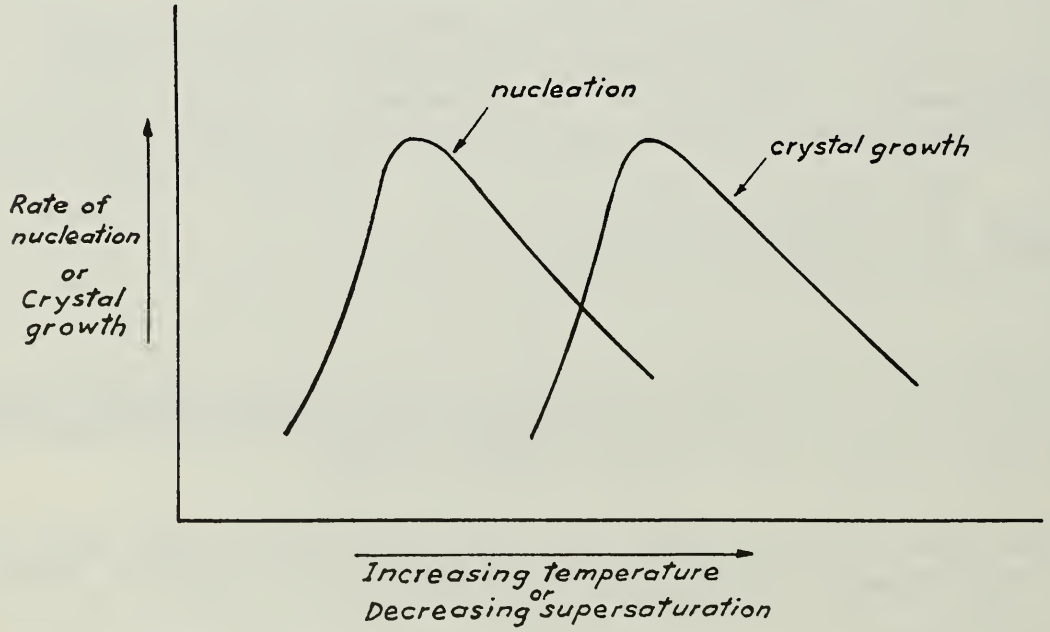
$$dN/dt \cdot 1/v = k_n C^n$$

the term dN/dt . 1/v represents the number of nuclei formed per unit time and per unit volume. C is the degree of supersaturation expressed in concentration units. n is the reaction order. The rate of nucleation also depends on the impurities and/or ingredients added, the degree of agitation and the presence of seed crystals.

The rate of nuclei formation increases very rapidly with increases in the degree of supersaturation or decreasing temperature within certain ranges for each. The rate drops sharply at a lower temperature due to an increase in viscosity.

The rate of crystal growth in terms of weight increase per unit surface, dM/dt . 1/S, is also proportional to absolute supersaturation, or with decreasing temperature; it then drops off, again due to the low diffusion rate at a higher viscosity. The peak maximum in the nucleation curve usually takes place at a lower temperature than that for the crystal growth curve as shown in Figure 1.

Figure 1



It should be noted that at a given degree of supersaturation, both the rate of nucleation and the rate of crystallization increase with increasing temperature.

For a given saturated sugar solution, the faster the rate of nucleation, the greater the number of nuclei formed, and the smaller the size of the final sugar crystal. Von Weimarn's equation relates the final crystal diameter, d, to the degree of supersaturation, C, as follows:

$$1/d = K \cdot C/C_o$$

where K is a constant and C_o is the saturation solubility at a given temperature.

Production of specialty sugars with various functionality is achieved partly via control of the "retention time" of the process conditions at the peak maximum in both nucleation and crystal growth curves.

Another important design and operational variable for the process is the control of heat balance between the heat of crystallization and the latent heat of water evaporation during the transformation of liquid syrup to a solid sugar. The heat of crystallization at the elevated temperature can be estimated via conventional thermodynamic treatment of the heat of "reaction" at different temperatures.(2) The latent heat of water evaporation can be derived from the boiling point data of a highly concentrated syrup at various pressures.

Further details in the theoretical aspect of the process are described in the United States Patents 3,194,682, 3,365,331 and 3,642,535 assigned to Amstar Corporation.

PROCESS DESCRIPTION

The essence of the process has been described in patents assigned to Amstar Corporation by the inventors. A patent issued July 13, 1965, to Tippens and Cohen describes the process for making fondant-size crystals of sucrose agglomarates with the flavor of brown sugar. The Miller-Cohen patent, issued January 23, 1968,

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(2) Wall, F. T., Chemical Thermodynamics, W. H. Freeman and Co., San Francisco and London.

provides further details of the transformation process. Specific conditions for sugar crystallization, use of air, retention time, etc. were discussed. A third patent, issued to Graham, Fonti and Martinez on February 15, 1972, describes a modified process for the production of Di-Pac®, a tabletting sugar. The same transformation process also is being used for the production of Amerfond® and Bakerfond™ via control of process parameters and product formulation.

The process basically consists of an evaporator, nucleator/crystallizer, dryer, mill and screens.

The evaporator is operated at a temperature in the range 120° - 130°C, with or without vacuum, to produce a concentrated syrup having a solids content of 91 to 97% by weight. Concentrated syrup flows from the evaporator to the vapor-liquid separator where the vapor is removed by a barometric condenser and the syrup is fed to the nucleator/crystallizer.

The retention time of sugar in this unit ranges from 10 seconds to 120 seconds depending on the product desired.

Air is introduced into the nucleator/crystallizer to remove vapor released by the crystallization of material therein due to the heat of crystallization. The air flow rate ranges from 9 to 40 cubic feet per minute per pound of sugar product per minute. If desired, a dual temperature air system can be used during the nucleation and/or crystallization phases to further maximize the process flexibility and efficiency.

The sugar product in aggregate form, leaving the nucleator/crystallizer with a moisture content ranged from 0.5% to 2.5%, is fed to the dryer for further drying if needed. The resulting dried aggregates are then supplied to a cooler where they are reduced in temperature to about room temperature. The sugar aggregates are then milled and screened to meet product screen specifications.

In general, the physical characteristics and functionality of the desired transformed products not only determine the selection of operating conditions, but also affect the design and therefore, the capital and operating costs of the process.

Before discussing the applications, let me show you what transformed sugar looks like as compared to regular sugar crystals.

(The authors did not supply photographs suitable for printing.)

PRODUCT CHARACTERISTICS AND APPLICATIONS

At the present time, Amstar has on the market four Industrial Specialty Sugars that are produced on the system just described. These products are Di-Pac®, a direct compaction tabletting sugar; Amerfond®, a fondant sugar for the candy industry; Bakerfond™, a fondant sugar for the baking industry and Brownulated® which is sold as a general purpose sugar with the flavor properties of brown sugar but with free-flowing characteristics. The Brownulated® is further divided into a granular and a powdered form.

The above-mentioned products possess two characteristics in common:

1. They are all dry fondant sugars.
2. They are all direct compaction tabletting sugars.

A cream fondant as used in the candy and baking industry is a paste consisting of a suspension of very fine crystals. The size of the crystals is such that when the paste is ground between the teeth, there is no sensation of grit. In general, we say that any particle of 40 micron size or less will not produce this gritty feeling. All of the specialty sugars mentioned before are made up of crystals which are below 40 microns in size and therefore, qualify as fondant sugars. In fact the majority of the crystals formed are in the range of 5-10 microns.

These crystals as formed in our process are bound to one another partly by the moisture remaining in the product and partly by non-sucrose if present and so form aggregates which are carefully screened and sized to more easily perform their intended function. The combination of small crystals and the air spaces between them as they form their individual aggregates makes these products ideal for direct compaction sugars.

Although all of the specialties mentioned possess two general characteristics, we do not position them in the trade in that manner. Individually, they are more suited for specific purposes as we shall demonstrate.

The specialty products are made from blends of liquid sucrose and specially selected additives. The additive has two distinct roles in the production of these items. The first role of the additives is to inhibit premature crystallization, thus allowing crystallization to take place where we want it. The second role played by these additives is to greatly enhance the functionality of the end products.

In the case of Amerfond® and Bakerfond™ used extensively in the candy and baking industry, the additive we use is invert sugar. Our finished product in both cases contains 5% invert on a dry basis. Invert sugar functions as a humectant which is essential in cream centers and icings. Also in the candy industry, cream centers contain an amount of invert that makes the fondant pliable enough to shape but still firm enough to extrude. The 5% invert in our Amerfond® serves the purpose admirably. Of course, the user adds invertase to the fondant so that some time after the creams have been coated, more invert will be formed and the creams will become more palatable. In the baking industry, Bakerfond™ is used in the preparation of quality icings As mentioned, it imparts humectant qualities to the icings but at the same time, it produces a highly desirable sheen or lustre to the finished product.

Bear in mind that the traditional manner for making fondants remains long and complicated and is more of an art than a science. Using Amerfond® and Bakerfond™, the production process becomes the simple addition of water to either one of the products and mixing for five minutes. The resulting fondants are easily reproducible and of excellent quality. Since the invert acts as a humectant, it becomes apparent that these two products are hygroscopic to some degree and for this reason we do not recommend them to the pharmaceutical trade as a tabletting excipient.

Di-Pac® is the product which we sell to the pharmaceutical industry as a direct compaction sugar. By using Di-Pac®, the user eliminates the conventional, lengthy process of wet granulation or slugging in the making of tablets. He simply adds an active ingredient such as a vitamin mix to our Di-Pac® with the necessary amount of lubricant, blend for the appropriate number of minutes and feeds the dry blends to the tabletting press. Because of the dextrin additive that we use in the initial liquid sucrose-additive blend, the resulting tablets possess excellent hardness. Of equal importance is the fact that the tablets are very non-hygroscopic which adds greatly to the stability of the active ingredient. We do not recommend Di-Pac® as a fondant sugar because the dextrin delays the wet-out time of the fondant preparation as compared to Amerfond®

or Bakerfond™. When we make Brownulated®, the additives of choice are those non-sucrose solids commonly found in soft sugar. Here again, these non-sucrose solids act first as a crystallization inhibitor and then perform their secondary role of providing a unique complimentary flavor adjunct to certain classes of icings.

As one can see, Amstar has gone well beyond the relatively simple sugar transformation process and through it applied technology research has developed a family of specialty sugars serving the present and future need of the food industry.

CONCLUSION

In this presentation, we have demonstrated that Amstar has a viable commercial process for transformation of various sugar liquors, with or without additives, directly into a dry sugar and sugar-containing products which have gained wide acceptance by the trade. We have had two decades of manufacturing and R & D experience with the process.

DISCUSSION

R. Cormier: (Redpath) What type of evaporator do you use?

D. Tippens (Amstar): This is a Blaw Knox "rising-falling" film evaporator. The feed goes into the center bundle of tubes at the bottom. A mixture of liquor and vapor emerge in a plenum at the top. All the vapor and the liquor that is now boiling are forced down the outer rows of tubes to the bottom discharge and vapor separator. You get a very high heat transfer coefficient because of the high velocity of the liquor propelled by the steam. From the vapor separator the concentrated liquor is pumped out to the crystallizer processor.

R. Cormier: When concentrating the feed, how do you decide it has reached the desired concentration? What do you monitor then?

C. C. Chou: We monitor the temperature. The brix is difficult to measure at that high level.

R. Cormier: Because of the possibly varying composition of the feed syrup how do you set the target final temperature?

C. C. Chou: We know exactly the composition of the feed, and therefore the temperature.

R. Cormier: Is this saying that, from that knowledge of the composition of the feed, you have a theoretical or empirical correlation allowing you to set the temperature to be reached?

C. C. Chou: Right. And one type of temperature measurement is not enough. We have several different types of temperature measurement right in that same area to confirm one another.

R. Cormier: Is the concentration done under vacuum?

C. C. Chou: We use six inches of vacuum, although this can vary depending on the products needed. However, we can run without vacuum, and with vacuum up to 13-in.

R. Cormier: But does not the use of vacuum at very high concentration represent a source of trouble?

D. Tippens: My initial patent on that process describes a "critical right triangle." The triangle appears in a plot on which its horizontal base represents a particular syrup concentration or evaporator discharge brix, scaled on the ordinate; its vertical side (to the right) represents a temperature, scaled on the abscissa; and its hypotenuse, a function of the vacuum level employed in the evaporator, completes a triangle, all points within which are safe for operating. The hypotenuse is a boundary, different for each level of vacuum employed, representing a specific degree of syrup supersaturation for all operating points of brix and temperature along it. Crystallization will occur in the evaporator tubes prematurely at operating points above this hypotenuse. Unfortunately, the points composing the hypotenuse must be determined experimentally for each feed material of different composition - meaning a lot of evaporator tube cleaning early in the game.

Ideally, you wish to operate at a vacuum high enough to minimize syrup temperature at the lowest workable brix level. An operating triangle for a given feed syrup is made up by first selecting the desired syrup concentration and drawing the triangle's base line, representing that concentration. Now, an hypotenuse, representing a particular operating vacuum is selected from the experimental data, which will intersect the triangle's base line at a point a little to the left of the most desirable syrup temperature. Now you complete the triangle by drawing its right vertical side at the maximum permissible syrup temperature. Operation then can be conducted at any point of brix and temperature within the triangle, the higher and farther to the left, the better; but with increasing risk of premature crystallization as you move.

R. Cormier: In the course of the work described have you found any specific components present in a feed syrup that did prevent it from being transformed though a look at its general characteristics would have let you believe it to be transformable according to your past general experience of the process?

C. C. Chou: We can transform a sugar liquor blend of down to 80 purity easily. It is a matter of throughput rate.

R. Cormier: Such a low purity figure surprises me.

C. C. Chou: Many people do not think that you can transform at that purity. You can transform liquor at that purity at a reduced flow rate.

IMPROVED 100 °S POINT AND POL

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ABSTRACT

A newly constructed polarimeter, and highly purified sucrose were used to redetermine the hundred degree point of the saccharimeter scale at 546 nm wavelength. The result differs from previously reported results by 140 to 500 ppm. In addition to the low pressure mercury discharge lamp, lasers at 546 nm and 633 nm wavelengths have been advantageously employed as polarimeter light sources. Lasers improved the sensitivity, accuracy and reproducibility of measurements and decreased the measurement time. These and related investigations open the door to future improvements in the determination of the pol of technical sugars.

INTRODUCTION

Pol, the optical rotation in "sugar degrees" (°S) of a defined solution of a sugar (raw, molasses, refined, etc.), measured under defined conditions, is ultimately based on the optical rotation of a solution of pure sucrose. A conventional definition of the solution, the conditions for measurement, and reliable artifact standards were the subject of much discussion and research from the 1840's to the 1930's (1). In 1932, agreement was reached at the 8th Session of the International Commission for Uniform Methods of Sugar Analysis (ICUMSA) (2) and the International Sugar Scale was established. The basis of the scale, the 100 °S point, was defined as the optical rotation of an aqueous solution containing 26 grams of sucrose per 100 ml, measured at 20 °C in a tube 200 mm long. A secondary definition was also given in terms of the optical rotation of crystalline quartz, thus continuing the use of quartz plates as artifact standards. The methods of sucrose purification, impurity analysis and optical rotation measurement were so reliable that this value of the 100 °S point remained unchallenged for over 30 years.

The advent of automatic polarimeters revived interest in the definition and the rotation value of the 100 °S point. Under the vigorous leadership of

Professor F. Schneider, Institut für Landwirtschaftliche Technologie und Zuckerindustrie (ILTZ), Braunschweig, Germany, the 100 °S point definition was scrutinized in the light of technological advances since 1932 (3). Measurements were undertaken to redetermine the rotation value of the 100 °S point. The methods of sucrose purification and impurity analysis were very similar to those used by Bates and Jackson (4) in the earlier measurements. An automatic polarimeter facilitated the optical rotation measurements. The result agreed with the 1932 value (5). In 1970 (6), the definition of the 100 °S point was altered to conform with the International System of Units, effecting a 0.001 percent increase in the rotation value.

The development of a more reliable method of analysis for moisture in sucrose (7) triggered another series of thorough measurements, which resulted in a rotation value 0.03 percent greater than the 1932 value (8,9). Before adopting the new 100 °S point value, ICUMSA required verifying measurements in another laboratory. The United States National Committee on Sugar Analysis (USNCSA) therefore promoted a joint venture between the National Bureau of Standards (NBS) and the International Sugar Research Foundation, Inc. (ISRF). Work began in September 1975, funded primarily by the Sugar Association of the United States and the National Bureau of Standards. We report here the results of that work to date, leaving details of procedures and instrumentation to a more lengthy paper (11). Also reported are the results of some work with quartz control plates, the artifacts by which the sugar scale is communicated to saccharimeter users. Attempts are then made to forecast the effects that our results and innovations will have on practical saccharimetry.

EXPERIMENTAL

Chemistry

The details of sucrose purification, analysis of impurities, and polarimeter design are described elsewhere (7,10-15). We would point out, however, that the aim of the analytical methods was to determine the amount of each impurity in the specially purified sucrose to ±3 to 9 ppm. The impurities included moisture, invert sugar, oligosaccharides (raffinose, kestoses, stachyose), ash, polysaccharides and other large molecules, and insoluble matter. Solutions of the sucrose were prepared by weight, rather than volume, because of the impracticality of measuring volume accurately to a part per million. The presence of microorganisms in solutions of the sucrose was monitored.

Polarimeter Design

The desired measurement sensitivity of 5 μrad imposed exceptional limits on all design aspects of the polarimeter. The procedural and instrumental accuracy requirements which will be treated in detail elsewhere (11), are summarized in Table I.

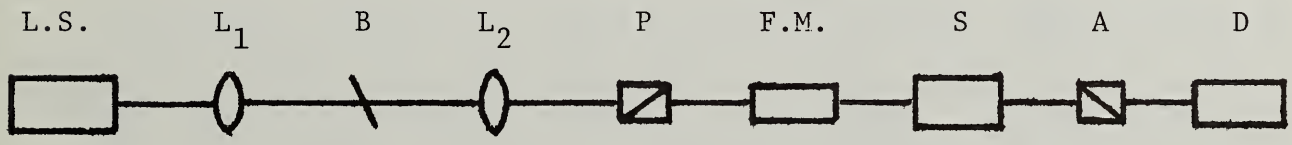
Figure I illustrates the basic components of the photoelectric polarimeter.

TABLE I

Polarimeter Design Criteria

	Desired	Reproducibility Achieved	Inherent Accuracy
Angle measurement	3 μrad	3 μrad	3 μrad
Temperature control	0.001°C	0.0005°C	0.001°C
Cell length	0.5 μm	0.1 μm	0.1 μm
Cell alignment	1.5 mrad	0.3 mrad	
Parallelism of cell windows	40 μrad	30 μrad	
Light beam divergence	4.4 mrad	0.2 to 4 mrad	
Wavelength	0.6 pm	(see text)	(see text)

Figure I
Polarimeter Schematic



L.S. = light source
L_1,L_2 = lenses
B = beam splitter to facilitate alignment
P = prism polarizer
F.M. = Faraday cell modulator
S = sample chamber
A = analyzer prism housed at the center of a rotating angle encoder
D = photodetector

Mirrors (not shown) allow a number of different light sources to be directed alternately down the light path of the polarimeter. The polarizer orientation is fixed. Modulation of the plane of polarization is accomplished by a 100 Hz sinusoidal current through the solenoid of a Faraday cell modulator. The analyzer is mounted in the rotor of a 21-bit optical encoder (least count equivalent to 3 microradians), which provides angle measurement. The polarimetric null point is determined with the aid of a frequency-selective amplifier (100 Hz) followed by a lock-in amplifier.

Up to six samples can be housed simultaneously in the thermostatted sample chamber, the temperature of which drifts less than 0.0005 °C per day. To assure temperature uniformity, the thermostatted chamber was made of aluminum with precisely bored holes into which the copper sample cells fit snugly.

Temperature is referenced to IPTS-68 with a platinum resistance thermometer that has been calibrated at NBS. The samples can be sequentially rotated within the sample chamber into the light path, maintaining alignment to about 0.3 milliradians. The polarimeter is located in an environmentally controlled room, where the air temperature varies less than 0.1 °C per day. Errors in measured optical rotation due to instrumental drifts have been determined by repeated measurements to be less than 3 microradians.

Light Sources

The emission at 546 nm of the atomic mercury spectrum from a low pressure, stabilized d.c. discharge in a Philips Type 93123* mercury discharge lamp was separated from the other mercury lines by use of a prism monochrometer and a special NBS filter pack. The latter was used previously for international round-robin measurements of quartz control plates. The filter's bandwidth at half the maximum transmittance is 10 nm. As another source of radiation at 546 nm, a stabilized tunable dye laser (Coherent Radiation, Model 599-21*) was tuned by means of the opto-galvanic effect (16) to emit the 546 nm wavelength. A helium-neon laser provided light with a wavelength of 633 nm. In the latter two cases, further filtering was not used.

Measurement Procedure

The sample chamber design allows six samples to be moved sequentially into the optical path. One sample was always air, and another was always a quartz control plate whose rotation had been measured at the National Physical Laboratory (NPL) England, Physikalisch-Technische Bundesanstalt (PTB) Germany, and NBS. In a typical measurement sequence, the sucrose samples were interleaved with air and the quartz plate samples, air being measured most often.

Density

The density of each solution was determined by comparison with two NBS liquid density standards (water and xylene) in a Mettler/Paar DMA 02D* Precision Density Meter.

Quartz Control Plates

The optical rotations of plates from the NBS collection and plates sent to us by various industrial users were measured at 546 nm wavelength (mercury discharge lamp) in the polarimeter which was constructed several years ago for that purpose (17). In the new polarimeter, on the other hand, the optical rotations of the plates were measured at a wavelength of 633 nm by employing several types of helium-neon lasers, from an inexpensive unpolarized laser to a servo-controlled single-frequency laser.

*The identification of commercial instruments is given only to describe fully the experimental phase of this work. In no instances does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the particular equipment described is necessarily the best available for the described purpose.

RESULTS AND DISCUSSION

100 °S Point of the Saccharimeter Scale

The 100 °S point is defined by ICUMSA recommendations (8):

> The "normal sugar solution" is defined as 26.0160 g of pure sucrose weighed in vacuo and dissolved in pure water at 20.00 °C to 100.000 cm^3. This corresponds to a concentration of 26.0000 g of sucrose weighed with brass weights in air under normal conditions (1013 mbar pressure, 20 °C, 50% relative humidity) in 100.000 cm^3 of solution at 20.00 °C. (Officially adopted at the 13th Session, 1962.)
>
> The basis of the 100 °S point of the "International Sugar Scale" is the optical rotation of the "normal sugar solution", as defined in Recommendation 1, at the wavelength of the green line of the mercury isotope ^{198}Hg (λ=546.2271 nm), 20.00 °C and 200.00 mm tube length. (Officially adopted at the 14th Session, 1966.)

In the Experimental section of this report we explained why our solutions were prepared by weight rather than by volume. From measurements of the densities of eleven sucrose solutions, the density of the normal sucrose solution was found to be 1097.641 ± 0.002 mg/cm^3 at a gravimetric concentration of 23.7017 g sucrose/100 g solution. From optical rotation measurements of nine solutions ranging from 23.4 to 24.1 percent sucrose, the optical rotation value of the 100 °S point was calculated with the aid of an equation for the concentration dependence of optical rotations of sucrose solutions (8). In computing the exact concentration of each solution, the total mass of impurities was subtracted from the mass of sucrose. The optical rotation due to optically active impurities was subtracted from the observed optical rotation of each solution. The resultant rotation value of the 100 °S point was 711.815 ± 0.087 mrad (40.784 ± 0.005 degrees of arc). This is compared with other reported values in Table II.

The history of the measurements prior to 1978 has been chronicled in the introduction of this report. Examination of the last four entries in the optical rotation column (α_{546}^{20}) leads one to the conclusion that the sucrose prepared in the U.S. is not identical to that prepared by ILTZ in Germany. The corrections made for impurities detected did not bring the rotation values into agreement. Indeed, dialysis of ILTZ sucrose at CSRRP in New Orleans revealed 50 ppm polysaccharides and other nondialysable substances for which ILTZ had not analyzed. On the other hand, ILTZ analysis of our sucrose revealed 40 to 60 ppm of oligosaccharide material which we had been unable to detect. Obviously more work is needed to characterize impurities in purified sucrose samples, and is presently underway in Germany and in the United States. Although measurements on both sugars agree that the presently accepted

TABLE II

100 °S Point Conditions

(26.0160 g/100 cm^3 at 20 °C)

Authors	Sucrose wt. %	Density	α^{20}_{546} (mrad)
Bates et al., 1932 (2)	23.7023	1.097614	711.45
Schneider, et al., 1963 (32)	23.7028	1.097594	
ICUMSA, 1966 (5)	23.7020	1.097629	711.47
ICUMSA, 1970 (6)			711.48
ICUMSA, 1974 (8)[b]	23.7017	1.097645	711.69
This report, 1978[a]	23.7017	1.097641	711.82
PTB, 1978 (18)[a]	23.7017		711.82
PTB, 1978 (18)[b]	23.7017		711.71

[a] USNCSA sucrose

[b] ILTZ sucrose

rotation value, 711.48 mrad, is not correct, ICUMSA recommended (18) that this value be retained until the differences between sugars could be resolved. Thus until further notice, the 100 °S point values officially remain (18,6):

$$\alpha^{20}_{546.2271\ nm} = 711.48\ mrad\ (40.765°)$$

and

$$\alpha^{20}_{589.4400\ nm} = 604.16\ mrad\ (34.616°)$$

Light Sources

Lamps

In all measurements discussed thus far, low pressure mercury discharge lamps provided light of wavelength 546 nm. Although a free atom at rest (i.e., at absolute zero) will emit light that is nearly monochromatic and which has excellent reproducibility, the atoms in practical lamps at higher pressure, higher temperature, and in the presence of an electrical discharge emit light which is polychromatic and is far from ideal for the purpose of sugar polarimetry. The thermal motion of the atoms and the collisions they induce in combination with the effect of the electric field necessary to maintain the discharge, broadens and shifts the wavelength of the emitted radiation in an extremely complicated fashion. It has been usual practice to adopt a conventional lamp structure in which the pressure, isotopic abundance, carrier gas and operating conditions are stipulated along with an optical procedure for

isolating the desired radiation from the total radiation of the lamp. Only in this way can the measurements using classical radiation sources from different laboratories be rationalized, since optical rotatory power is inherently dispersive.

For certification of quartz control plates and for basis measurements for the 100 °S point, the use of a low pressure discharge lamp has been recommended (19). However, in measurements of one 23.7 percent sucrose solution and 2 quartz control plates, we observed as much as a 0.01 percent range of rotation values, depending on the method of isolating the 546 nm mercury line of the recommended lamp. A similar effect has been observed by Steel and Wilkinson (20) with electrodeless mercury-198 lamps such as those that are used as standards for length interferometry. A shift of 0.03 nm (5 parts in 10^5) in mean wavelength causes a shift of 0.01 percent in the optical rotation of quartz or sucrose at 546 nm. Representative filter bandwidths are typically about 10 nm.

Helium-Neon Lasers

A gas laser, such as the very common helium-neon laser, is free of many of the disadvantages associated with spectral lamps. The radiation emitted, even from an inexpensive helium-neon laser, is more reproducible and more monochromatic than the conventional discharge lamp. In addition, the absence of a continuum of background radiation obviates the necessity for additional line isolating optical elements. The effect of the finite, but small, bandwidth is not detectable by our polarimeter. Some practical additional benefits are gained by the use of the laser: its greater light intensity and lower noise facilitate much more sensitive polarimetric measurements and its natural spatial coherence permits typical light beam divergence angles to be 1 to 2 mrad. Ten-fold reduction of the divergence angle can be accomplished easily with simple optics.

We have therefore employed lasers as light sources in the measurement of the optical rotations of quartz control plates. Table III compares the results obtained with several different lasers. The wavelengths of these lasers may differ by as much as a few parts in 10^6. No significant differences are seen

TABLE III

Comparison of Helium-Neon Lasers

	Optical rotation at 20 °C (mrad)		
Description	#1	#2	#1727AB
Unpolarized	415.066	519.432	11.481
Unpolarized	415.065	519.442	11.468
Polarized	415.058	519.434	11.464
Lamb-dip stabilized, polarized	415.059		
Average	415.062	519.436	11.471
Std. Deviation	0.004	0.005	0.009
Typical measurement σ	0.01	0.01	0.02

TABLE IV

Comparison of Mercury Lamp and Helium-Neon Laser

Plate #	Plate age (years)	$\alpha_{546}/\alpha_{633}$	Relative standard deviation x 10^5 Lamp	Laser
1	74	1.366268	4	2
244	67	1.366253	3	2
1724	13	1.366309	3	2
1725	13	1.366294	2	2
1726	13	1.366378	5	7
1727A	13	1.366451	8	5
1727B	13	1.366350	8	7
Average		1.366329	5	4
σ		0.000069		
$(\sigma/\text{Avg})\times 10^5$		5		
Reference 22		1.366262		

in the optical rotation measurements. In Table IV, measurements using a helium-neon laser (wavelength of 633 nm) are compared with measurements using a mercury lamp (546 nm wavelength), by means of the optical rotation ratio ($\alpha_{546}/\alpha_{633}$). The "relative standard deviation" (4th and 5th columns) is the standard deviation of several measurements divided by the mean optical rotation of those measurements. The magnitude of relative standard deviation is affected by characteristics of the plates. The newer plates seem to show a slightly larger optical rotation ratio than the older plates. Still, the consistency of the optical rotation ratio supports the conclusion of Bünnagel and Spiegelhalter (22) that the origin of optically pure, correctly manufactured quartz control plates does not significantly affect their optical rotatory dispersion. Furthermore, the determination of the optical rotation of a quartz control plate at 632.991 nm (vacuum wavelength of the helium-neon laser) should be sufficient to certify its rotation within 0.01 percent at any other wavelength for which the optical rotation ratio is known.

Laser at 546 nm

Because the green line of ^{198}Hg, 546.2271 nm vacuum wavelength, has been a reference wavelength for so long, a laser which provides 546 nm light would be very desirable. Working mercury lasers have been reported (23). Such a device is under construction at NBS, but has not yet been completed. In the meantime, we have used a stabilized, tunable, single frequency dye laser to provide 546 nm light. We have exploited the optogalvanic effect (16) in order to define the dye laser wavelength to within 0.002 nm. For polarimetry, the dye laser provides all the same advantages as does the helium-neon laser, with the added flexibility of wavelength tunability.

TABLE V

Optical Rotation of QCP #1724

Light Source	α_{546}^{20} (mrad)	σ (mrad)
Lamp (24, 25)	679.314*	0.010
Lamp (this work)	679.314	0.014
Laser (this work)	679.390	0.005

*Average of measurements at NPL (England), PTB (Germany), and NBS (Ref. 24,25).

In Table V, dye laser illuminated polarimeter measurements are compared with lamp illuminated measurements. The dramatic difference is well outside the limits of measurement error. The rotation difference, 0.076 mrad, corresponds to a wavelength difference of 0.03 nm. In light of the foregoing discussion, it is reasonable to assume that the wavelength of the lamp (low pressure discharge, natural isotopic abundance) is responsible. However, at the PTB in Germany the effective vacuum wavelength of the lamp was found to be 546.228 nm (26) by measurement of the optical rotation of a 50 mm long quartz rotator whose optical rotatory dispersion had been previously calibrated (21). NBS and PTB are currently working to find the cause of the difference between measurements made using lamps and lasers.

PRACTICAL SACCHARIMETRY

Because of the commercial significance of pol determinations, there is a tendency to judge the significance of pol-related research from an economic point of view. The impact of the probable redefinition of the 100 °S point is impressive. Although we are not yet certain, the new value could be as much as 0.34 mrad, or 0.048 percent higher than the presently used value. This means, for example, that a sugar which pols 96.00 °S on the present scale, would pol only 95.95 °S. There is actually less sucrose in a given sugar than is presently assumed. In terms of the world sugar trade, 0.05 percent represents about 20 million dollars annually. It is indeed very important that the 100 °S point be founded on a sound scientific, internationally acceptable basis.

A change in the definition of the hundred degree point would immediately antiquate present saccharimeter scales and calibration tables. Rather than retooling scales of saccharimeters presently in use, however, a new calibration factor could be calculated. A minor change in a computer chip could bring new digital saccharimeter displays into conformance with the new scale. The widespread use and availability of inexpensive calculators minimizes the need to produce new detailed conversion tables.

Given a reliable 100 °S point, the accuracy, reproducibility, and speed of pol determinations in the technical laboratory is the next economic concern. Several factors which can affect the accuracy of polarimetric results are listed in Table VI. The values for weight, volume, and cell length parameters are based on 100 mL total solution volume and 200 mm cell length.

TABLE VI

Magnitude of Error Factors which can cause 0.01 °S Error in Pol of 100 °S Solution

Sucrose Weight	2 mg
Solution Volume	0.008 mL
Solution Weight	8 mg
Saccharimeter Scale	0.01 °S
Effective Wavelength	0.024 nm
Temperature in Polarimeter	
of Solution	0.2 °C
of Quartz Control Plate	0.7 °C
Cell Length	0.02 mm
Birefringence	(see text)
Color of Solution	(see text)
Turbidity of Solution	(see text)
Clarification Effects	(see text)

In Table VI, both solution volume and solution weight are listed. Even though the 100 °S point is defined in terms of solution volume and solutions are presently routinely prepared volumetrically, we expect that gravimetric solution preparation will eventually dominate sugar laboratory routine. There are several practical reasons for preferring a gravimetric procedure over one which requires volumetric solution preparation:

(1) The entire amount of water (solvent) required can be added to the sugar sample immediately after weighing the sugar, while the flask is still on the balance. One need not add only part of the water, then wait until the solution has been mixed and its temperature has returned to room temperature (or the temperature at which the volumetric flask was calibrated) before returning to add the last few drops of water, and mix again.

(2) Expensive, breakable volumetric flasks could be replaced by less expensive, even unbreakable plastic bottles.

(3) The routine gravimetric measurement is more accurate than the routine volumetric (meniscus) measurement, allowing better possible agreement between parallel determinations.

(4) A stirring magnet could be in the flask or bottle throughout the gravimetric process to facilitate mechanical mixing. This is impossible in a volumetric procedure.

(5) Because volumetric solution preparation in the sugar labs is really semi-gravimetric (the sugar is weighed), conversion to full gravimetric would involve only a slight change in procedure. No new equipment need be purchased.

(6) Since 1966 the dependence of optical rotation on sucrose concentration and on solution temperature has been defined in terms of gravimetric

solution concentration (5). Since then, measurements of optical rotation of gravimetrically prepared solutions have been combined with measurements of density to define the rotation value of the "normal sucrose solution" (the 100 °S point).

Conversion to a procedure incorporating gravimetric preparation of solutions can decrease analysis time, improve reproducibility, decrease equipment cost, and harmonize with methods which are used to determine the basis of the sacccharimeter scale. A gravimetric pol method has been described by Hopewell and Wilson (27).

Birefringence results in an observation of apparent optical rotation when the cell is filled with air or pure water. Theoretical calculations show that the magnitude of the apparent optical rotation depends on cell window characteristics, magnitude and distribution of physical stress on windows, orientation of the major stress axis of each window with respect to the plane of polarized light incident on each, the magnitude of sample optical rotation, and the birefringence characteristics of other optical elements in the polarimeter (polarizer, Faraday cell modulator). R. J. King has described some details of these effects (28,29). Our derivations (11) lead to a slightly different theoretical expression than King's, but the general qualitative conclusions are the same. One cannot even be certain that subtraction of the optical rotation of the empty or water-filled cell from that of the solution-filled cell will yield the correct optical rotation value for the solution (unless polarimeter and cell birefringence are negligible). This is probably the reason that ICUMSA Method 1 for the polarization of raw sugars suggests rotating the cell 90 degrees between each of five optical rotation readings (30). The optical rotation of the solution is then calculated as the average of the readings (minus the polarimeter zero), the effects of birefringence being thereby cancelled. The problems resulting from birefringence are not clearly understood, however. Much more work is needed.

Solution color can alter the effective wavelength by unevenly absorbing wavelengths passing through the solution. Turbidity reduces the intensity of light which is transmitted by the solution, thereby decreasing measurement sensitivity and increasing measurement error. Clarification, on the other hand, while reducing color and turbidity effects, can introduce errors as large as 0.5 °S (27).

Perhaps the most exciting prospects for the future will derive from work with lasers. Many researchers have recognized the beneficial effects use of lasers could have on polarimetry. ICUMSA has tentatively accepted the helium-neon laser as a reference light source for the measurement of quartz control plates (31). Helium-neon and krypton lasers have been used in measurements of the rotatory dispersion of pure sucrose solutions (9) and technical sugar solutions (18). As a direct result of our work, ICUMSA has urged that the use of dye lasers for the adjustment of reference wavelengths in polarimetry be studied (18).

Of the many available lasers, the helium-neon laser will likely be the first to be used routinely in sugar polarimetry because of its low cost, compact size and reliability. The problems associated with wavelength

uncertainty will thereby be essentially eliminated: the effective wavelength will not vary significantly from source to source, polarimeter to polarimeter, or lab to lab, nor will it be significantly affected by optical rotatory dispersion or color of samples. The decrease in polarimetric sensitivity due to turbidity and color will not be as serious with a laser because of its much greater initial intensity. Furthermore, Rayleigh scattering is about half as intense at 633 nm as at 546 nm and colorants in technical sugar solutions do not absorb as strongly at 633 nm as they do at 589 or 546 nm. Especially with short pathlength cells, clarification might be unnecessary. From the point of view of polarimeter manufacture, the helium-neon laser would obviate the need for collimation optics and would allow replacement of photomultipliers by less expensive silicon photodiodes. Although microradian polarimetric sensitivity has been demonstrated, accurate inexpensive methods of measuring such angles need to be devised before microradian polarimeters could become a commercial reality.

There are some problems associated with laser polarimetry which are as yet unresolved. The optical rotation of clarified technical solutions relative to sucrose is not the same at 633 nm as at 546 or 589 nm (18). This is to be expected and must be thoroughly investigated before a uniform method of treating pol measurements at 633 nm can be established. Other potential problems stem from coherence of light, forward scattered light, reflections, and birefringence. All of these, except coherence, occur with conventional light sources, but their effects on polarimetric measurements can be more successfully investigated with lasers.

Much farther in the future the mercury-198 laser may become such a commercial reality that rapid two-wavelength polarimetry will become routine. Even simultaneous dichromic polarimetry will be a distinct possibility. The introduction of lasers into the sugar analysis laboratory promises to improve accuracy, reproducibility, speed, and efficiency of sugar polarizations as much as did the introduction of the automatic saccharimeter.

Acknowledgements

Linda Wheelock (Holly Sugar Company, Colorado Springs, Colorado) prepared specially purified sucrose samples and developed analytical methods for determination of glucose, fructose, and raffinose. Earl Roberts (Cane Sugar Refiners Research Project, New Orleans, Louisiana) determined amounts of polysaccharide and other large molecules in the purified sucrose. Analyses for ash were performed at Redpath Sugar Co., Ltd. (Montreal, Canada) and at C&H Sugar Co. (Crockett, California) under the direction of Claude Gagnon and Stuart Patterson, respectively. John Sullivan (Revere Sugar Co.), Dr. Lorna Sniegoski and Rafael Espinosa-Leniz helped with analyses for glucose, fructose and raffinose at NBS. Dr. Dennis Reeder (NBS) monitored microorganism levels in sucrose solutions. Dr. W. Bruce Olson (NBS) provided valuable advice concerning the design of the polarimeter as did Dr. Richard Spanier (Rudolph Research).

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F. G. Carpenter (CSRRP): What do you see as the possibility for this in polarization measurements. You intimated that the red light would be better. Is it more expensive? How much more expensive is it than a plain old mercury light we have all been using? You say it is speedier, how much more precise is it?

A. L. Cummings: With the He-Ne laser one can read optical rotation more rapidly and precisely. Measurements that we have made on quartz control plates, for example, have demonstrated that in about 1/4 the measurement time, measurements with the He-Ne laser can be about twice as reproducible (i.e. the standard deviation is about half as large) as measurements with the mercury lamp. When, on the other hand, we attempted to measure as rapidly with the mercury lamp as we can with the laser, the measurement uncertainty was about 20 times as large.

Another exciting prospect with lasers derives from the fact that the light is so intense and so monochromatic. Polychromatic rotation, in other words the measurement of the rotation at several wavelengths simultaneously, is truly feasible. For example if the mercury laser is successfully commercially developed, it would be very feasible to shine both the mercury laser and the He-Ne laser at the same time through the polarimeter and with the proper detection system, which has already been conceived and published, you could measure optical rotation at two wavelengths simultaneously. Dr. Howard Layer, one of the coauthors of this report, recently developed a laser which simultaneously emits five wavelengths. So with a prism at the back of the polarimeter following the analyzer one could simultaneously measure the optical rotation at five wavelengths. That has a nice application. This morning we have been hearing how terrible optical rotation is in deciding how much sucrose is really there. It is true! But if you take optical rotation at several wavelengths, then using the optical rotary dispersion of sucrose and of the other impurities that are present, you could conceivably, with a small computer calculation, deconvolute from that data how much sucrose, glucose, fructose, and each other rotating impurity were present.

In the paper we have a table in which four different H-Ne lasers are compared. Reading down the table, the respective purchase prices were $115, $225, $450, and $8000. They all gave the same rotation on several quartz plates to within the precision of our measurements. The light intensity of the least expensive laser was a little less stable than the other lasers, resulting in slightly poorer sensitivity of the measurement. Still, for our purposes, for calibrating quartz control plates, it gave sufficiently precise and accurate results. That $115 laser now costs $125. If you are building polarimeters and you don't want a nice case around it, the cost can be much less. A laser tube can be expected to last one to six years depending upon how it happens to live. The least expensive replacement tubes cost about $60. Replacement mercury lamps, on the other hand, cost around $95.

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